Catalysis Letters Vol. 99, Nos. 3–4, February 2005 (© 2005)
DOI: 10.1007/s10562-005-2096-6

Inhibition of dibenzothiophene hydrodesulfurization by di-aza heterocycles

Teh C. Ho* and J. Sobel

Corporate Strategic Research Laboratories ExxonMobil Research and Engineering Co. Annandale, NJ 08801

Received 23 August 2004; accepted 30 September 2004

The hydrodesulfurization of dibenzothiophene over a sulfided $CoMo/Al_2O_3$ catalyst can be severely inhibited by 1,10-phenanthroline. The catalyst's hydrogenation activity is totally suppressed and cannot be fully recovered upon stripping of adsorbed nitrogen species. The bulk of the hydrogenolysis activity is suppressed but can be completely recovered upon stripping. Implications of these observations are discussed, including the possibility of a chelating-enhanced adsorption mechanism.

KEY WORDS: Hydrodesulfurization; Catalyst poisoning; Nitrogen compounds; Di-aza Heterocycles; Mono-aza Heterocycles.

1. Introduction

Indigenous nitrogen species in petroleum distillates have long been known to inhibit catalytic hydrodesulfurization (HDS) of organosulfur species. Recently, this effect has received much attention because governments worldwide are mandating substantial sulfur reduction in refinery products such as diesel and gasoline. For instance, the sulfur specification for on-road diesel in the U.S. is 15 ppmw in 2006, down from the current 500 ppmw.

A fair amount of research has been done on the inhibiting effects of six- and five-membered nitrogen heterocycles containing only one nitrogen atom per molecule, or mono-aza heterocycles [1] and references therein]. To the best of our knowledge, no work has been reported on the inhibiting effects of heterocycles containing two nitrogen atoms. Such di-aza heterocycles are present in diesel fuel, for instance, benzo[c]cinnolines [2]. Di-aza heterocycle structures are different from those of mono-aza heterocycles as do reactivities. In this study we use 1,10-phenanthroline (PN) as a probe molecule with which to gain some understanding of the inhibiting effects of di-aza heterocycles in diesel HDS. The reaction considered is the HDS of dibenzothiophene (DBT) over a commercial sulfided $CoMo/Al_2O_3$ catalyst.

2. Experimental

PN, DBT and tetralin are available commercially (Aldrich). The composition and physical properties of the $CoMo/Al_2O_3$ catalyst are: CoO, 3.5%; MoO_3, 12.5%; nitrogen BET surface area, 285 m^2/g; and Pore volume, 0.52 cc/g. Prior to use, the catalyst was crushed and sieved to 20–40 mesh granules and then sulfided at 360 °C for 1 h at atmospheric pressure with a 10% H_2S-in-H_2 gas mixture. The catalyst charge was 2.5 cc.

Reactions were conducted in a vertical fixed-bed reactor made of a 3/8 in i.d. 316 stainless-steel pipe. It was equipped with a calibrated feed burette, pump, gas–liquid separator, and product collector. In all runs a large excess of hydrogen was used, corresponding to a gas-to-liquid ratio of 32 k mol H_2/m^3 liquid feed. Two feed solutions were used. Feed A is a 10 wt% solution of DBT in tetralin. Feed B contains 0.8 wt% PN and 10 wt% DBT in tetralin. The operating conditions were 325 °C, 6 LHSV, and 3.1 MPa total hydrogen pressure.

The sequence of the poisoning experiments is as follows. The reactor was started with feed A to provide steady-state HDS data prior to poisoning by PN. Following this, feed A was replaced with feed B at time zero at the same conditions. After the reactor reached a new steady HDS level, feed A was put back on stream to strip reversibly adsorbed nitrogen species off the catalyst, thus recovering all or part of the lost HDS activity. The state of the reactor was monitored by intermittently analyzing the liquid effluents throughout the entire experiment.

Virtually no partially hydrogenated DBTs (e.g., tetrahydro-DBT) were detected in the liquid effluents (by GC/MS). Besides H_2S, the main HDS products were identified to be biphenyl (BP) and cyclohexylbenzene (CHB). Hence, as is well known in HDS catalysis, there are two apparent HDS pathways. The hydrogenolysis path gives BP through direct sulfur extraction. The hydrogenation path produces CHB through prehydrogenation of one of the aromatic rings. The relative importance of these two paths may be roughly gauged by a hydrogenation index γ defined as the concentration

[1]Retired
* To whom correspondence should be addressed.
E-mail: teh.c.ho@exxonmobil.com

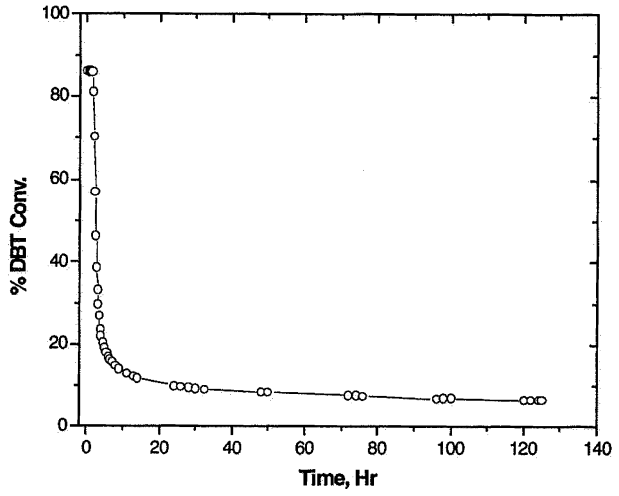

Figure 1. DBT percentage conversion vs. elapsed h after introducing the PN-containing feed; 325 °C, 6 LHSV, 3.1 MPa, and 32 k mol H_2/m^3 liquid feed.

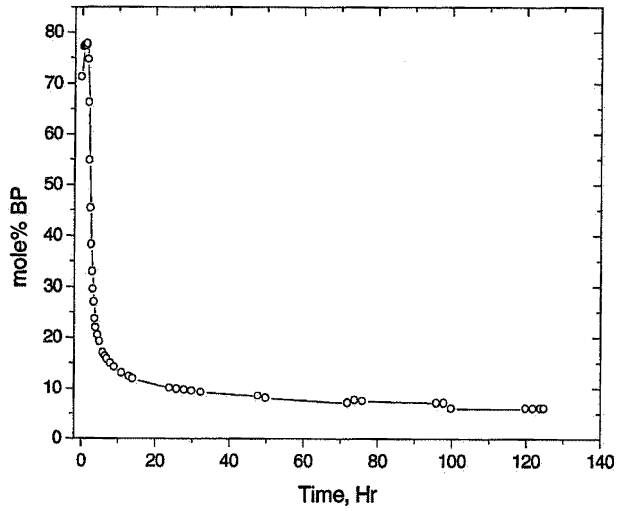

Figure 3. BP mole percent vs. elapsed h after introducing the PN-containing feed; 325 °C, 6 LHSV, 3.1 MPa, and 32 k mol H_2/m^3 liquid feed.

ratio of CHB to BP in the liquid effluent, that is, γ = (mole % CHB)/(mole % BP).

3. Results

Figure 1 shows the percentage of DBT conversion as a function of elapsed hour after switching to the PN-containing feed. The conversion is at a high 85% prior to the feed switching. It drops almost vertically right after the poisoning experiment commences. The corresponding mole percents of CHB and BP in the liquid product are plotted in figures 2 and 3, respectively. Figure 2 shows that the hydrogenation pathway is completely suppressed. Figure 3 indicates that the hydrogenolysis pathway is also substantially suppressed, but a small fraction of the hydogenolysis sites survive the PN attack. As can be seen from figure 4, initially γ is about 0.12, indicating that the hydrogenolysis pathway is heavily favored. The value of γ rapidly drops to zero immediately after the start of the poisoning experiment. Hence, the poisoning process is selective toward the hydrogenation sites. On an absolute basis, the hydrogenolysis sites are also hit very hard in that the BP concentration in the liquid product drops precipitously from about 80% to less than 10%, as figure 3 shows.

Figure 2 reveals a square wave pattern for PN adsorption on hydrogenation sites. The adsorption rate on these sites is so fast that a breakthrough time can hardly be determined on the scale shown in figure 2. This says that the sharp PN concentration wave front propagates rapidly through the bed. Figure 3 shows that the adsorption of PN on hydrogenolysis sites behaves similarly.

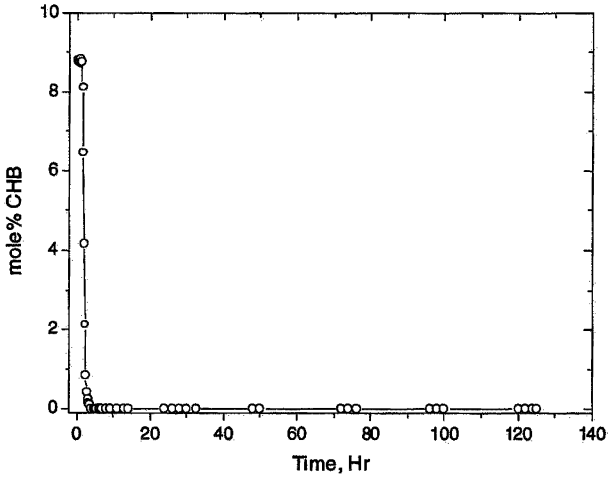

Figure 2. CHB mole percent vs. elapsed h after introducing the PN-containing feed; 325 °C, 6 LHSV, 3.1 MPa, and 32 k mol H_2/m^3 liquid feed.

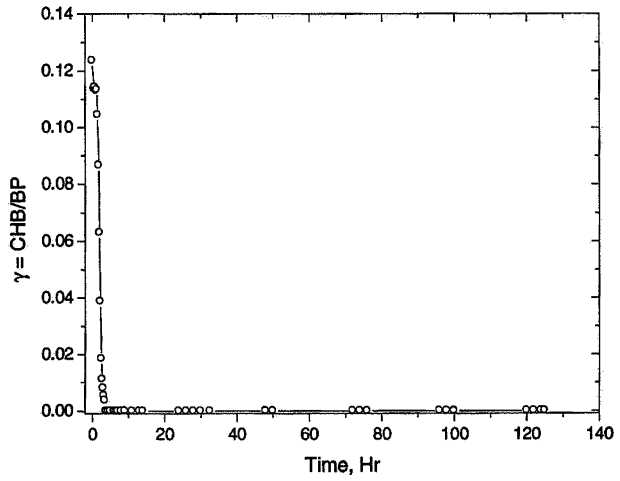

Figure 4. Value of γ vs. elapsed h after introducing the PN-containing feed; 325 °C, 6 LHSV, 3.1 MPa, and 32 k mol H_2/m^3 liquid feed.

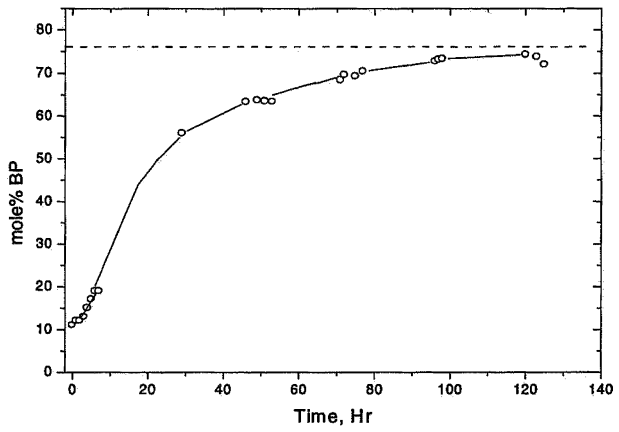

Figure 5. BP mole percent vs. elapsed h after stripping with feed A; 325 °C. 6 LHSV, 3.1 MPa, and 32 k mol H_2/m^3 liquid feed. Dashed line: original activity level.

A key difference between the two types of active sites can be seen from subsequent stripping experiments. After switching back to feed A, the lost hydrogenolysis activity can be completely recovered after 120 h, as shown in figure 5 in which the horizontal dashed line represents the original activity level. In contrast, the response of the hydrogenation activity to the stripping is slower, as figure 6 shows. In fact, the bonding between the adsorbed nitrogen species and the hydrogenation sites appears to be so strong that no recovery of the hydrogenation activity was observed during the first 10 h of stripping. Moreover, the hydrogenation activity does not come close to its original level even after 120 h. This may have much to do with the propensity of nitrogen heterocycles to polymerize and may eventually go on to form coke [3, 4]. The sluggish desorption behaviors displayed in figures 5 and 6 indicate that the adsorbed nitrogen species, whether on the hydrogenation or hydrogenolysis sites, are quite "sticky."

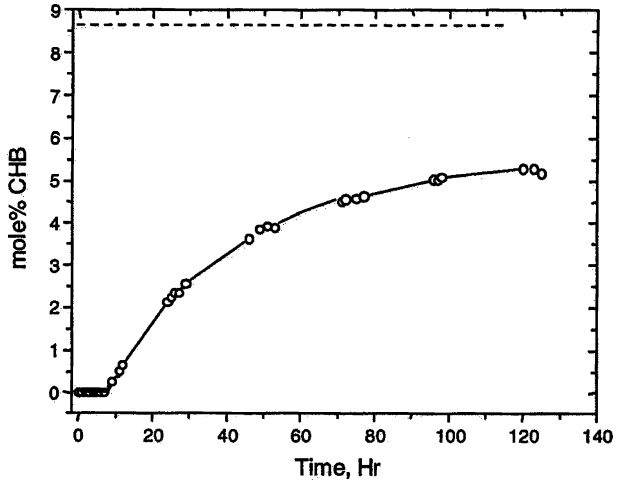

Figure 6. CHB mole percent vs. elapsed h after stripping with feed A; 325 °C, 6 LHSV, 3.1 MPa, and 32 k mol H_2/m^3 liquid feed. Dashed line: original activity level.

4. Discussion and conjectures

Besides being more basic than its mono-aza analogs (e.g., phenanthridine), PN may be viewed as a bidentate chelating ligand capable of strong, preferential binding with a catalytically active site (e.g., exposed Mo atom). Presumably, its preferred adsorption configuration involves the two pyridinic nitrogen atoms. This is depicted in figure 7 where "*" represents an active site. Our proposition here is that the presence of the second nitrogen atom enhances the binding ability of PN. This chelating-enhanced bonding may explain the observed fast, strong adsorption of PN. In the organometallic chemistry literature [5–7], there are numerous examples of σ- and π-complexes of five- and six-membered nitrogen heterocycles.

For six-membered multi-ring mono-aza nitrogen compounds (e.g., quinolines, acridines), the evidence has been that the ring-hydrogenated, but not denitrogenated intermediates (e.g., tetrahydroquinolines, octahydroacridines) are largely responsible for the inhibiting effects in the HDS of DBT [8,9]. Assuming that a parallel exists here, We surmise that PN's hydrogenated derivatives (e.g., octahydro-PN), being bidentate chelating ligands as well, may well be more inhibiting than PN itself.

A different situation may arise with cinnolines, a class of di-aza-heterocycles in which the two nitrogen heteroatoms are in the same ring (also called diazines). Here the chelating-enhanced adsorption argument may not apply. Take benzo[c]cinnolines as an example, the two nitrogen atoms may possibly bind two different sites, as figure 8 shows schematically. The binding strength of this one-site-per-nitrogen mode, presumably, is weaker than that of two-sites-per-nitrogen mode depicted in figure 7.

Figure 8 may be taken as suggesting that diazines may be more inhibiting than mono-aza-heterocycles of comparable size on a per molecule basis. But this may or may not be the case on a per nitrogen atom basis. In practice, the nitrogen content of petroleum distillates is generally measured as ppmw of nitrogen atom. It is of practical interest to know how the poisoning potency of

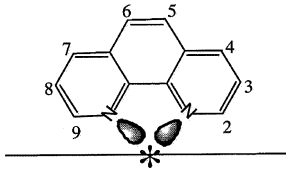

Figure 7. Proposed binding of the two nitrogen atoms in 1,10-phenanthroline with an active site denoted by "*".

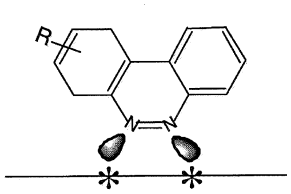

Figure 8. Proposed binding of the two nitrogen atoms in benzo[c]cinnolines with two active sites denoted by "*".

a di-aza heterocycle stacks against that of a mono-aza heterocycle of comparable size on a per nitrogen atom basis.

The foregoing consideration focuses on the end-on adsorption mode (σ-complex formation). The possibility of the side-on adsorption (π-complex formation) cannot be ruled out with certainty. If the end-on mode is more important than the side-on mode under HDS conditions, then the relative positions of the two nitrogen atoms in a di-aza-heterocycle molecule may play a role in determining the molecule's inhibiting power. As an example, one of the two nitrogen atoms in a bi-aza-heterocycle could even be harmless if the two nitrogen atoms are far away from each other diagonally, e.g., the 2 and 7 positions in PN. This point is worthy of further study.

5. Conclusions

The HDS of DBT can be severely inhibited by di-aza-heterocyc1es, possibly due to a chelating-enhanced adsorption that is fast and strong. The process appears not to be completely reversible. As a result, di-aza-hetrocycles are potentially potent coke precursors. Possible mechanisms are proposed. Further work in this area should contribute to the ultimate understanding of how nitrogen heterocycles inhibit HDS.

Acknowledgment

Thanks are due to Professor A.R. Katrizky for helpful discussions.

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