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CONTROL OF CATALYTIC HYDROTREATING SELECTIVITY WITH AMMONIA

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The focus of our attention has now shifted to the effect of ammonia on hydrodeoxygenation (HDO) of selected model compounds. Scouting studies with 2-phenylphenol (OPP), phenyl ether (PE), 3-ethylphenol (MEP) and dibenzofuran (DBF) indicated some inhibition of hydrogenation activity but with OPP, PE and MEP several products were formed that were not completely identified and kinetic analysis would be difficult. We therefore focussed on DBF, with which we have had some experience, and we carried out a series of studies at 3.5 MPa and 360°C. H₂S was generated in situ and NH₃ was introduced as supercooled liquid by an ISCO pump to constitute 12 kPa in the reactor. Samples of reaction products were analyzed by g.c. using a 30-m Supelcowax (high polarity) column.

Present experimental results are shown on Figures 2-5. From a previously published study we have developed the reaction network for the HDO of DBF as shown on Figure 1. This is the basis for our interpretation of present data. The HDO of the DBF network follows two pathways. There is a hydrogenation route where single-ring products predominate, mostly cyclohexane and cyclobenzene. The other path is a hydrogenolysis route where double-ring compounds predominate, mostly cyclohexylbenzene (CHB), biphenyl (BP), and dicyclohexyl (DCH). Figure 2 shows a plot of percent dibenzofuran (DBF) remaining versus space time. Based on this plot, ammonia seems to have no apparent effect on the overall rate of HDO of DBF. Figure 3 shows that there are more double-ring products in the presence of ammonia (based on one datum at high space time), and Figure 4 shows more single-ring products in the absence of ammonia. This seems to indicate that ammonia inhibits hydrogenation activity, while not affecting the overall rate of HDO of DBF.

Further evidence of hydrogenation inhibition is observed in Figure 5 which shows

a plot of the percent of initial DBF converted to dicyclohexyl (DCH) versus space time. Dicyclohexyl is a direct product of the hydrogenation of cyclohexylbenzene. From Figure 5, we see that there is less DCH product in the presence of ammonia, indicating a suppression of hydrogenation activity, although the concentration differences are small. A similar effect of ammonia on the hydrogenation of propylbenzene was observed by Gultekin et al. [1984].

Problems Encountered and Future Work

We had thought that direct injection of NH_3 might be preferable to indirect generation in situ from propyl amine, but at these very low NH_3 flow rates we found that the accuracy with which the pump delivers liquid NH_3 is questionable. We are therefore somewhat uncertain about the true NH_3 partial pressures in the reactor in the data obtained thus far. In addition high pressure drops appeared at low space times caused by partial plugging of the reactor which caused difficulty in reproducing data. This may have been caused by by-products from the oxygenated compounds used in the scouting studies or catalyst aging. A new catalyst batch will be used for the next set of studies with DBF and NH_3 will be generated in situ from propyl amine added to the feed instead of injection of NH_3 as such. This should give better control of NH_3 partial pressure.

References

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Figure 1. Proposed hydrodeoxygenation network of dibenzofuran (LaVopa and Satterfield, 1987)

Figure 2 The effect of 12 kPa of ammonia on the hydrodeoxygenation of dibenzofuran.

Figure 3. The effect of ammonia on double-ring product distribution in the HDO of DBF.

Figure 4. The effect of ammonia on single-ring product distribution in the HDO of DBF.

Figure 5. The effect of ammonia on the formation of dicyclohexyl from the hydrogenation of cyclohexylbenzene.

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