Polymer formation during the HDN of indole

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During kinetic studies of the hydrodenitrogenation (HDN) of indole (IND) over a NiMo/P–Al_2O_3 catalyst, it was found that material balances (representing loss of indole) were often low and varied depending on reaction conditions. Tests of IND with an alumina support, in which no reaction to HDN products occurred, also gave low material balances, which appeared to reach a line out value with space time. UV spectra of a liquid sample from this run showed evidence of species different than IND, which is attributed to a polymer. The low material balances were due to the failure of the GC analysis to detect the polymer in the product sample and possible loss of polymer by condensation in the lines leading to the sample collector. Material balances with the catalyst were related to conversion of IND to HDN reaction products. Low material balances were only obtained with IND, not with reaction products alone. It was concluded that the loss of IND is due to formation of a polymer. At low space time (low IND conversion), the polymer is rapidly formed in competition with conversion of IND to HDN products, while at high space time (high IND conversion), the polymer decreases due to back reaction to IND, followed by conversion to HDN products. The consequence of polymer formation, when it occurs, is that it represents a parallel reaction path to conversion of indole and needs to be accounted for in any kinetic analysis of the HDN of indole.

Keywords: hydrodenitrogenation, indole, polymer, material balance, NiMo catalyst

1. Introduction

In many reaction studies, material balances are sometimes not routinely obtained. Without the confirmation of a material balance, reaction rates and product selectivities cannot be certain. In particular, if a polymer of the reactant or adduct product is formed and not detected or analyzed in the exit sample, account must be made for this in any kinetic analysis. This may be important in reactions involving organic nitrogen and oxygen compounds, which are prone to form polymers under certain reaction conditions.

In studies of quinoline hydrodenitrogenation (HDN), Yang and Satterfield [1] reported a material balance loss of about 10% and the “reactor pressure gradually dropped and finally the reactor became completely plugged”. They found this occurred with 5,6,7,8-tetrahydroquinoline in the feed and suggested a trimer was responsible. Yang et al. [2] recently reported severe material balance losses during the HDN of piperidine. As these increased with increasing hydrogen sulfide in the feed, they ascribed the loss to an acid–base reaction, leading to insoluble amine sulfur compounds in the liquid product.

In our studies of the kinetics of HDN of indole, we consistently encountered some poor material balances. We present here our further study and interpretation of this phenomenon.

2. Experimental

The catalyst used consisted of a 4% NiO and 24% MoO_3 supported on alumina containing 2% P (Topsøe TK-555). Two γ-alumina samples were also tested, one containing only alumina and the other the support for the catalyst, containing 2% P. The extrudates were crushed and screened to 40- to 60-mesh particles. Runs were carried out in a fixed-bed flow reactor under vapor-phase conditions at a total pressure of 38 atm, maintained by a back-pressure regulator. A 0.25 g sample of catalyst was mixed with 5 cm^3 of glass beads and presulfided with a 10% H_2S/H_2 mixture at atmospheric pressure and 400 °C for 2 h. The liquid feed consisted of 0.25–0.75 wt% indole (99+%), 1.0 wt% dimethyldisulfide (DMDS) and 0.5 wt% n-decane (as internal standard) in n-heptane (all by Aldrich). Liquid feed rates were 5–24 ml/h and H_2 rates were 100–450 cm^3(STP)/min. After aging the catalyst for two days to achieve line out, liquid samples were taken and analyzed by GC, using an OV-17 column with FID. Repeat samples at a given standard condition demonstrated that after about 40 h on stream the catalyst activity did not change over 400 h of operation. Liquid product samples were always clear and colorless. The only compounds found in greater than 1% yield were: indole (IND), indoline (HIN), *ortho*-ethylaniline (OEA), *ortho*-ethylcyclohexenes (ECHE), *ortho*-ethylcyclohexane (ECH), and ethylbenzene (EB). Indoline was always present, but in very low concentration (less than 2% of IND), and is considered a reactant, together with IND. All other compounds are considered products from reaction of indole, i.e., carbon–nitrogen hydrogenolysis (CNH) products. CNH conversion in this context refers to all products from IND in which one or two C–N bonds are broken, i.e., OEA, ECHE, ECH and EB. CNH conversion is not the same as HDN conversion, which only includes non-N-products.

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The material balance, b, was determined by taking the ratio of the molar amounts of the sum of the GC products divided by decane in the sample to the ratio of IND divided by decane in the feed, viz.

$$b = \left(A_{\mathrm{d}}^0/A_{\mathrm{IND}}^0\right)(1/A_{\mathrm{d}})\sum m_i A_i, \tag{1}$$

where A_{d} is area of the decane peak, and A_{IND} the area of the IND peak in the reactor sample, with superscript 0 denoting the respective areas in the feed sample; A_i is the area of all the individual peaks in the sample, with m_i being their molar factors with reference to IND. Material balances were generally ± 0.03, except at the lowest temperature of 310 °C, at which considerable scatter was obtained.

The CNH conversion from the GC analysis does not account for loss of IND from the material balance. In order to obtain the correct mole fractions present in the reactor under reaction conditions, the following equations can be derived assuming a polymer (POL) of n molecules of IND:

$$y'_{\mathrm{POL}} = (1-b)f/nb, \tag{2}$$

$$y'_{\mathrm{CNH}} = f y_{\mathrm{CNH}}, \tag{3}$$

$$y'_{\mathrm{IND}} = f y_{\mathrm{IND}}, \tag{4}$$

$$x'_{\mathrm{T}} = y'_{\mathrm{POL}} + y'_{\mathrm{CNH}}, \tag{5}$$

$$f = nb/\left[1 + (n-1)b\right], \tag{6}$$

where y_{CNH} and y_{IND} are mole fractions obtained from the GC analysis, and y'_{POL}, y'_{CNH} and y'_{IND} are mole fractions corrected for polymer, x'_{T} is the total conversion of IND, and f is a correction factor to account for loss of IND.

3. Results

3.1. Preliminary observations

During studies of the reactivity of indole over the catalyst under various reaction conditions, it was observed that in material balances (mole balance on IND) were continually low, far outside of experimental error. Balances were especially low at lower temperatures. The low balances appear to represent a true loss of IND or its reaction products somewhere throughout the reactor system.

The low balances are not due to continual coke formation, as the coke content of the catalyst after one run of 466 h was 3.0% C and after another run of 344 h was 2.4% C. These values are comparable to those obtained in previous short-time tests with IND (about 30 h), and the catalyst activity was stable after two days on stream. The catalyst after the 344 h run gave a N/C atomic ratio of about 9, close to the ratio of 8 for indole, suggesting that the coke consisted predominantly of a polymer of indole. Also, near the end of one run, the pressure upstream from the reactor gradually increased, and mole balances were consistently lower. Increasing the hydrogen flow rate temporarily alleviated the situation.

The loss in indole may be due to higher molecular weight material, as very small peaks beyond the IND peak were observed in the GC samples, which might be attributed to a dimer or trimer of IND. However, these peaks were not sufficient to account for the relatively large material balance losses. Furthermore, when conditioning the GC column, it was noted that material gradually eluted as the temperature was raised. Therefore, it appears that the low balances were due to some species associated with IND or its products. A liquid sample from the run with alumina (see below) was analyzed by UV spectroscopy, together with a blank of IND in heptane at the same concentration. The GC analysis of the sample showed only IND present and gave a material balance of 0.88, representing a significant loss of IND. The UV spectra, given in figure 1, show clear evidence of two distinct peaks in the sample not found in the IND blank. These peaks, shifted to higher wave lengths, would be indicative of a higher molecular weight species, e.g., polymer. Also, a plug of glass wool, placed in the

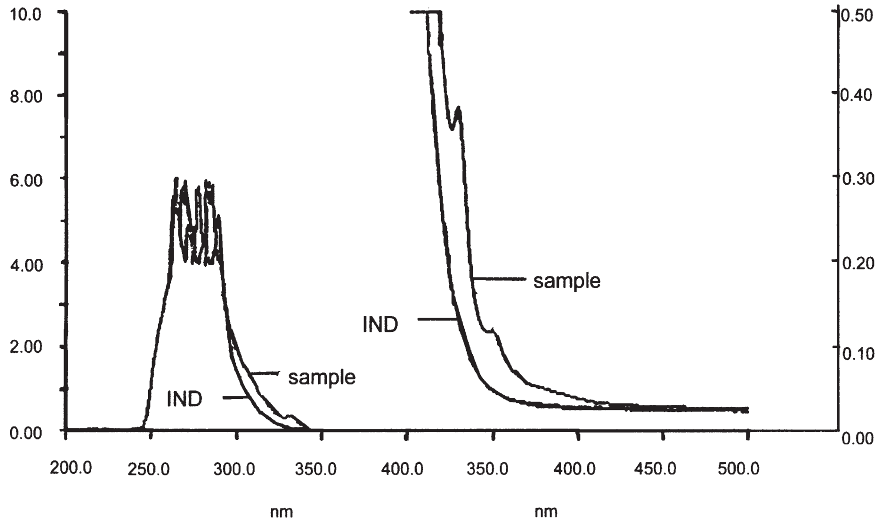

Figure 1. UV spectra of sample from alumina run.

tubing at the exit of the reactor, showed the presence of a small amount of a carbonaceous material after an extended run period of 212 h. Thus, it seems reasonable that the loss of IND could be due to deposition of an IND polymer in the lines after the reactor, as well as in the liquid sample.

3.2. Material balances

3.2.1. Material balances without catalyst

The results of an IND run with alumina at 340 °C are shown in figure 2(a) as material balance vs. space time (tau) for three different IND feed concentrations. The interesting feature of this plot is the small effect of space time on the material balance with indication of a line-out value. This indicates an apparent approach to equilibrium in polymer formation, i.e., in addition to forming polymer, there is evidently a back-reaction in which POL decomposes back to IND, as only IND and very small amounts of indoline were detected in the products, i.e., no CHN products were formed. Another significant result is that the fraction of POL is inversely related to the concentration of IND in the feed. Since the low material balance is due to the loss of IND (or HIN) and thus related to the yield of polymer, if the polymerization reaction were homogeneous (not catalytic), then the POL yield should increase with increase in the IND concentration in the feed, not decrease as observed. Therefore, this result implies that the polymerization reaction is catalytic in nature, presumably due to the acidic character of the alumina, as polymerization reactions are generally acid catalyzed. A separate test during this run using HIN in place of IND gave 20% HIN left and 80% IND formed (exclusive of POL), showing the reversibility of the $\mathrm{IND} + \mathrm{H_2} \rightleftharpoons \mathrm{HIN}$ reaction. Interestingly, the test with HIN gave a high material balance of about 0.97, despite there being 80% IND present. Apparently, the presence of a relatively high concentration of HIN inhibited POL formation, perhaps through its stronger adsorption on the active alumina sites.

For an IND run with the P/alumina support, figure 2(b) also shows that the material balance seems to be reaching a limiting value. This support gave a material balance of 0.82 at 340 °C, compared to a material balance of 0.88 for the alumina support under the same conditions. Thus, it would appear that the presence of P in the support increased polymer formation, although we cannot be certain in view of the variability in material balance values and the possibly different acidic nature of the aluminas. An IND run with only glass beads gave good material balances, showing that the POL formation was not due to a homogeneous reaction. Tests without H_2S present gave material balances not appreciably different than when H_2S (via DMDS) was present. Also, it is significant that tests with ethylcyclohexane and *ortho*-ethylaniline gave material balances close to one, indicating that our collection and analysis techniques are not the source of low material balances.

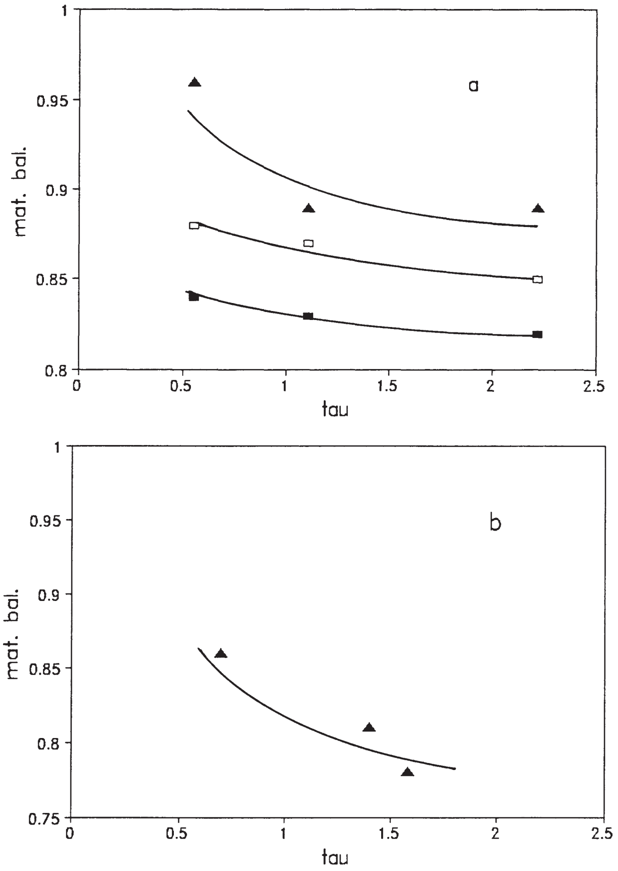

Figure 2. Material balance vs. space time, tau (kg min/m^3) for reaction of IND over: (a) Alumina support. Temperature 340 °C. (■) 0.25, (□) 0.5 and (▲) 0.75% IND in liquid feed. (b) P/alumina support. Temperature 360 °C; 0.67% IND in liquid feed.

In summary, these results indicate that, under HDN reaction conditions, a polymer of IND appears to be formed over the alumina support. The polymer is only formed from IND (and/or HIN), not by HDN reaction products. The reaction is catalytic and rapid, leading to an equilibrium concentration of polymer.

3.2.2. Material balances with catalysts

In one run with the NiMo catalyst, indole conversion data were obtained at three IND feed compositions and various space times, both at 325 and 340 °C. Material balances varied between 0.8 and 0.9, depending on reaction conditions. In analyzing the data for a trend, a rough correlation was found with uncorrected CNH conversion ($1 - y_{\mathrm{IND}}$), as shown in figure 3, suggesting that the material balance is related to the IND conversion. Since the material balance can be related to the polymer mole fraction in the gas phase in the reactor via equations given above, the minimum polymer possible is a dimer. Assuming POL as a dimer, the data of figure 3 are replotted in figures 4 and 5 in terms of mole fractions of POL (y'_{POL}) and CHN products (y'_{CHN}) versus total conversion of IND (x'_{T}, includes POL). The starred data points are for the respective CNH products (y_{CNH}) and IND (y_{IND}) without correction for POL, i.e., values obtained directly from the GC analyses, and

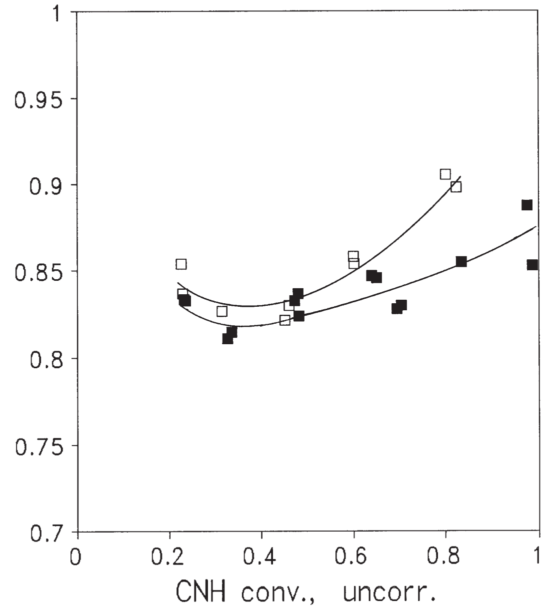

Figure 3. Material balance vs. uncorrected CNH conversion. (□) 325 °C; (■) 340 °C.

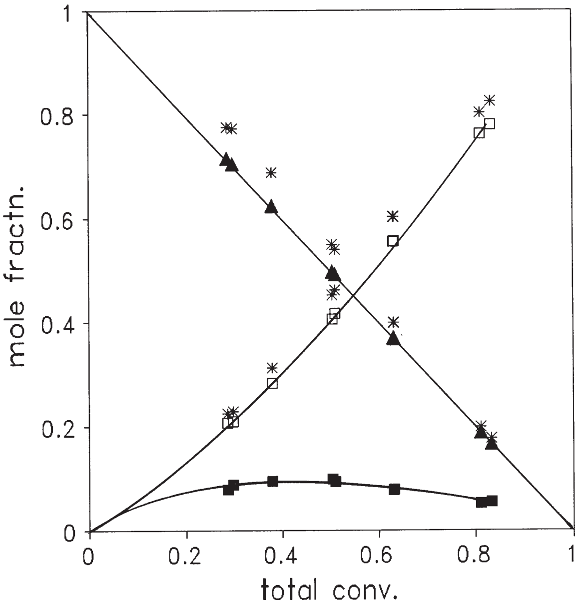

Figure 5. Mole fraction vs. total conversion of IND over NiMo catalyst at 325 °C. (□) Corrected CNH products; (▲) corrected IND; (■) dimer; (∗) respective uncorrected values.

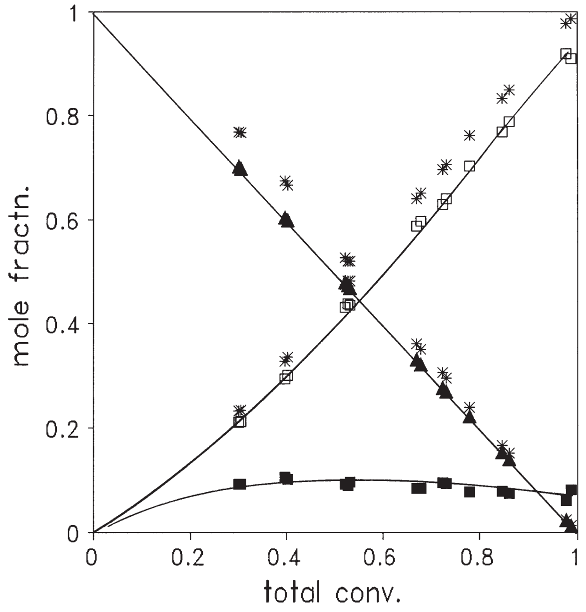

Figure 4. Mole fraction vs. total conversion of IND over NiMo catalyst at 340 °C. (□) Corrected CNH products; (▲) corrected IND; (■) dimer; (∗) respective uncorrected values.

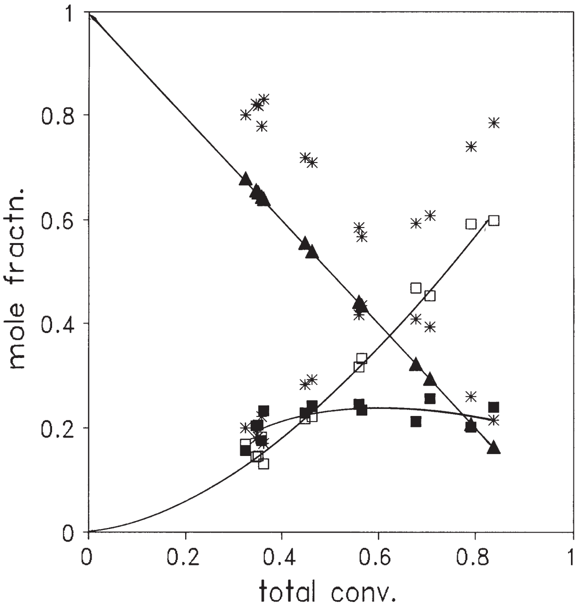

Figure 6. Mole fraction vs. total conversion of IND over NiMo catalyst at 310 °C. (□) Corrected CNH products; (▲) corrected IND; (■) dimer; (∗) respective uncorrected values.

will be discussed later. These plots show that, as conversion increases (increase in space time), the yield of POL increases and then decreases. Thus, it appears that as IND undergoes HDN, the amount of POL decreases from decomposition back to IND, which is then further reacted to CNH products. Similar results will be obtained if the POL is a trimer; only the mole fraction of POL will be lower and that of CNH products proportionally higher. Thus, with active catalyst present, the POL decreases with IND conversion, in contrast to the results with alumina where an equilibrium level is attained.

In another run with the catalyst, indole conversion data at various space times were obtained at 310 °C and two inlet IND feed concentrations. Plots of mole fractions of POL, IND and CNH products versus total conversion are given in figure 6, again assuming the polymer to be a dimer. In contrast to the above results at higher temperatures, now the polymer only slowly decreased with conversion at this temperature. Figure 7 displays the same results in terms of space time. This plot indicates that the CNH reaction is considerably faster than the POL back-reaction, with the

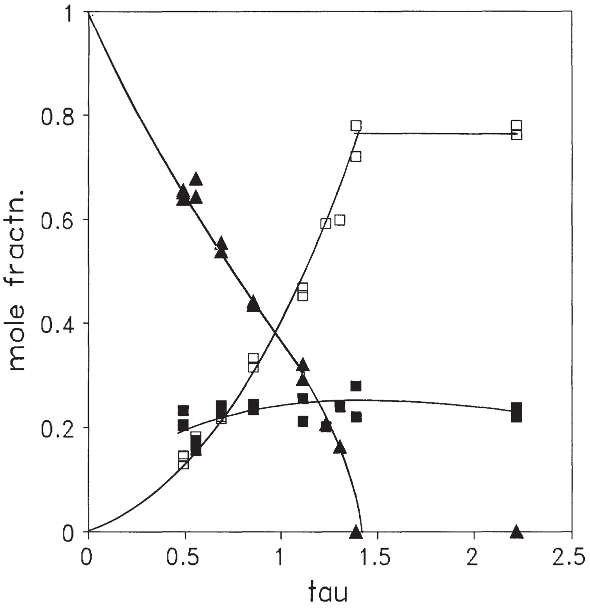

Figure 7. Mole fraction vs. space time, tau (kg min/m^3) for reaction of IND over NiMo catalyst at 310 °C. (☐) Corrected CNH products; (▲) corrected IND; (■) dimer.

result that, at high conversion, appreciable POL still exists. An interesting feature of this plot is that, even after all the IND had been completely converted to CHN products (only ethylcyclohexane and small amounts of ethylbenzene were left), the polymer only gradually decreased due to its very slow back reaction. Tests with only ethylcyclohexane in the feed gave no reaction and material balances close to unity both with the catalyst. Therefore, the residual polymers (from low material balances) in figure 7 at high space times are real.

3.2.3. General conclusions

(a) Material balances are based on analyses of liquid products obtained in the collection vessel. The GC analysis covers all significant products and indole, up to the retention time for IND. Since some of the polymer formed resides in the liquid product, any higher molecular weight products are not accounted for in the GC analysis. There is evidence of a number of small peaks in the GC beyond IND (<2% IND), but no significant peak that could be associated with a high-molecular weight compound. In any case, the current analysis adopted can give reasonable values of polymer formed in terms of total IND lost from material balance measurements.

(b) Unfortunately, the amount of POL formed is subject to some error, especially at lower temperature. This may be due to inherent variability of the reaction, which is very rapid, and to memory effects from slow adsorption/desorption rates of polymer from the catalyst surface.

(c) The polymer forms from IND (or HIN) and not from any HDN products. The reaction occurs on the alumina support and is reversible. It is not known whether it also occurs on the active NiMoS phase of the catalysts. The polymer yield decreases in the presence of the catalyst as IND is converted to CHN products. Therefore, polymer formation competes with CNH formation at low conversions of the latter, but becomes less important at high conversions, except at low temperature.

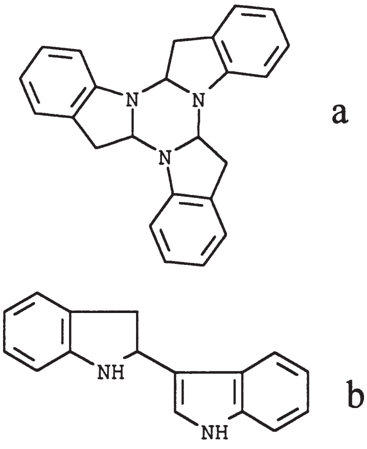

Figure 8. Possible dimer and trimer structures of IND. Adopted from (a) [4] and (b) [5].

4. Discussion

It may be supposed that the cause of poor material balances may be due to loss of light products in the H_2 exit stream from the back-pressure regulator. This has been ruled out for the following reasons: (1) The lightest CNH reaction product is ECH. Tests with feeds containing only ECH gave material balances close to one, showing that loss of ECH is negligible. (2) Lower molecular weight species may be formed from hydrocracking of CNH products. Runs with IND showed that polymer yield gradually decreased with IND conversion (figures 4 and 5), contrary to that expected for production of cracked products, where the yield of cracked products should increase with space time. Also, the run with alumina gave low material balances (figure 2), where no reaction of IND occurred and cracking products would be negligible. Thus the low material balances must be due to polymer formation.

Yang and Satterfield [1] proposed that plugging of their reactor during the HDN of quinoline was due to a trimer of partially hydrogenated quinoline. An indole polymer was reported in liquid products from the HDN of an indole-middle distillate feed [3]. Enamine forms of trimers of piperidine and pyrrole have been reported [4]. For indole, this might have the trimer structure depicted in figure 8(a). Dimer and trimer forms of indole [5] have also been reported. A picture of the indole dimer is shown in figure 8(b). It is interesting that the structure suggests an addition reaction between IND and HIN, connected through the carbon atoms of the N-ring. In our runs, there was always a small amount of HIN present together with IND.

The occasional increase in upstream pressure and plugging is likely due to deposition of the polymer downstream of the catalyst, but still in the heated zone, resulting in growth and dehydrogenation of the polymer to form a solid deposit. This could be similar to the deposit found on the catalyst, which by chemical analysis agreed well with a polymer of indole. Hadjiloizou et al. [6] have suggested an analogous trimer to that in figure 8(a) for piperidine, as possibly being a precursor to coke formation.

It is significant that polymer was obtained with alumina when CHN reaction products were absent. Thus, the polymer is not due to an addition reaction between IND or HIN and the intermediate amine, *o*-ethylaniline, analogous to secondary reactions reported for piperidine [7] and for pyrrole [8].

Liquid samples were always colorless, and contained some dissolved H_2S. Also passing H_2S through samples of IND or HIN in heptane failed to produce any change, and GC analysis showed no other peaks beside IND or HIN. Therefore, the polymer could not be due to a sulfur-type precipitate, as reported for piperidine [2].

From the results of this study, it is evident that polymer formation represents an additional mode of reactivity of indole, besides that leading to CNH products, viz.

$$\begin{tikzcd}
 & & \text{POL} \arrow[dl, shift left] \\
\text{IND} \arrow[r, shift left] & \text{HIN} \arrow[l, shift left] \arrow[ur, shift left] \arrow[dr] & \\
 & & \text{CNH Prods.}
\end{tikzcd}$$

Thus, over alumina, no CNH products are obtained, and the POL yield reaches an equilibrium with sufficient space time. However, with catalyst present, POL forms in competition with CNH products at low space time and then gradually decreases by back-reaction to IND, which further reacts to CNH products.

It is obvious that polymer formation will have an effect on the kinetics of the various steps in the HDN reaction. All CNH products corrected for polymer will be decreased by the factor f given in equation (6). For example, the data of figures 4 and 5 at higher temperatures show only slight differences in HDN products, whether corrected for polymer or not (starred points), since the mole fractions are small and within experimental error; while larger differences at lower temperature are evident in figure 6 due to more POL. However, these figures show appreciable differences between corrected and uncorrected values of IND at low conversions because of the relatively high mole fraction of IND. Thus, kinetic analysis with respect to disappearance of IND needs to include reaction to and back-reaction of POL, as well as reaction to CNH products. However, if the polymer is a trimer or higher, then its presence will have less effect on the HDN kinetic analysis.

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