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CONTROL OF CATALYTIC HYDROTREATING SELECTIVITY

WITH AMMONIA

Report for April 1, 1993 to June 30, 1993

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Repair work on the experimental equipment was completed in April and shake-down runs were carried out in early May with the assistance of Dr. Chung Lee, who made a second one-day visit to M.I.T. to provide guidance on bringing the equipment on stream and provide details on use and interpretation of the g.c. analytical equipment.

We have chosen as our standard reaction conditions: $T = 360^\circ$, total pressure about 6.9 MPa, partial pressure of PBz = 24.4 kPa, partial pressure of $H_2S = 13.3$ kPa, partial pressure of $NH_3 = 13.3$ kPa, space-time = 200 h. g. cat/mol PBz. The carrier liquid is hexadecane ($C_{16}H_{34}$). As before, the H_2S and NH_3 are generated in situ by hydrogenation of 1-dodecane thiol and n-propyl amine, respectively, added to the C_{16} feed.

The activity of the fresh catalyst dropped to a steady state level after about 120 hours on stream following which four runs were carried out at p.p. NH_3 values of 0, 13.3, 24.4 and 48.8 kPa, respectively. For each NH_3 p.p., space-times were varied at the following levels: 50, 100, 200, 400 and 600. Analyses were made for propylcyclohexene (CA), propylcyclohexane (CB) and benzene (CD). No other products were found in any significant amounts. The ratio CB/CD is a measure of the activity for ring hydrogenation relative to hydrocracking. The data are shown in four tables that follow.

The results will be analyzed kinetically in the next quarter. However, the following generalizations are evident: NH_3 significantly reduces the activity of the catalyst for both types of reaction. The activity for hydrocracking is reduced more than that for ring hydrogenation, a favorable result, but the effect is not large at the conditions studied thus far. The effect is most evident at low NH_3 concentrations.

In subsequent work similar runs will be carried out at $330^\circ C$ and $300^\circ C$, and the data will be analyzed kinetically.

RUN # 1

$T=360^{\circ}\text{C}$ $P_{\text{tot}}=6.9\text{ MPa}$; $P_{\text{PBz}}=24.4\text{ kPa}$; $P_{\text{NH}_3}=0\text{ kPa}$

$P_{\text{H}_2\text{S}}=13.3\text{ kPa}$

Carrier : n-Hexadecane (935.4.6 ml)
PBz : 0.24 mol/liter (=33.41 ml)
Propylamine : 0 mol/liter (=0 ml)
1-Dodecanethiol : 0.133 mol/liter (=31 ml)

Space time τ	C_A/C_{A0}	C_B/C_{A0}	C_D/C_{A0}
50	0.920	0.054	0.0095
100	0.860	0.103	0.0180
200	0.760	0.192	0.0341
400	0.580	0.341	0.0610
600	0.450	0.462	0.0800

RUN # 2

$T=360^{\circ}\text{C}$ $P_{\text{tot}}=6.9\text{ MPa}$; $P_{\text{PBz}}=24.4\text{ kPa}$; $P_{\text{NH}_3}=13.3\text{ kPa}$

$P_{\text{H}_2\text{S}}=13.3\text{ kPa}$

Carrier : n-Hexadecane (924.6 ml)
PBz : 0.24 mol/liter (=33.41 ml)
Propylamine : 0.133mol/liter (=10.91 ml)
1-Dodecanethiol : 0.133 mol/liter (=31 ml)

Space time τ	C_A/C_{A0}	C_B/C_{A0}	C_D/C_{A0}
50	0.990	0.0072	0.0008
100	0.980	0.0150	0.0015
200	0.960	0.0340	0.0030
400	0.932	0.0592	0.0059
600	0.903	0.088	0.0087

RUN # 3

$T=360^{\circ}\text{C}$ $P_{\text{tot}}= 6.9 \text{ MPa}$; $P_{\text{PBz}}=24.4 \text{ kPa}$; $P_{\text{NH}_3}=24.4 \text{ kPa}$

$P_{\text{H}_2\text{S}}=13.3 \text{ kPa}$

Carrier : n-Hexadecane (915 ml)
PBz : 0.24 mol/liter (=33.41 ml)
Propylamine : 0.244 mol/liter (=20 ml)
1-Dodecanethiol : 0.133 mol/liter (=31 ml)

Space time τ	C_A/C_{A0}	C_B/C_{A0}	C_D/C_{A0}
50	0.991	0.0065	0.000488
100	0.985	0.0129	0.000973
200	0.970	0.0255	0.001930
400	0.945	0.0506	0.003810
600	0.915	0.0749	0.005600

RUN # 4

$T=360^{\circ}\text{C}$ $P_{\text{tot}}= 6.9 \text{ MPa};$ $P_{\text{PBz}}=24.4 \text{ kPa};$ $P_{\text{NH}_3}=48.8 \text{ kPa}$

$P_{\text{H}_2\text{S}}=13.3 \text{ kPa}$

Carrier : n-Hexadecane (895.6 ml)
PBz : 0.24 mol/liter (=33.41 ml)
Propylamine : 0.488 mol/liter (=40 ml)
1-Dodecanethiol : 0.133 mol/liter (=31 ml)

Space time τ	C_A/C_{A0}	C_B/C_{A0}	C_D/C_{A0}
50	0.990	0.0061	0.00039
100	0.987	0.0121	0.00077
200	0.972	0.0240	0.00150
400	0.945	0.0476	0.00304
600	0.921	0.0705	0.00451

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