CONTROL OF CATALYTIC HYDROTREATING SELECTIVITY
WITH AMMONIA

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Experimental work continued with a series of runs (Runs #5-8) at 330°C and 6.9 MPa that utilized the same concentrations of PBz and H₂S as in the previous runs at 360°C. NH₃ concentrations and space-times were varied as before. One further run (Run #9) was made at 300°C and 13.3 kPa. This completes our experimental work.

The results of all 9 runs (those of the last quarter as well as this) have now been analyzed kinetically. The two reactions were treated as being each first order, i.e.,

where A = PBz, B = PCH and D = Bz. If the overall reaction is first order, then

$$-\frac{dC_A}{dt} = (k_1 + k_2) C_A \text{ and } -\ln \frac{C_A}{C_{A0}} = (k_1 + k_2) t$$

A plot of $-\ln C_A/C_{A0}$ versus space time should then give a straight line, as indeed it does for all runs. An example is shown on the attached Figure 1 for run #5.

To determine individual rate constants (k_1 and k_2), the following relationships hold for first order reactions:

$$C_B/C_{A0} = \frac{k_1(1 - C_A/C_{A0})}{k_1 + k_2}$$

and
$$C_D/C_{A0} = \frac{k_2(1 - C_A/C_{A0})}{k_1 + k_2}$$

Plotting C_B/C_{A0} or C_D/C_{A0} versus $1 - (C_A/C_{A0})$ yields a straight line with slope of $k_1/(k_1 + k_2)$ or $k_2/(k_1 + k_2)$ respectively. An example, again for run #5, is shown on Fig. 2. With the value of $(k_1 + k_2)$ from Fig. 1, k_1 and k_2 can each be determined.

The Appendix gives the raw data for all 9 runs, plus calculated values of $(k_1 + k_2)$, k_1 and k_2 for each run. The selectivity, $S = k_1/k_2$. Values at 360°C as a function of NH₃ partial pressure are shown on Figure 3 based on the data from Runs #1-4. The addition of NH₃ substantially decreases the overall rate (see values of $k_1 + k_2$ in the tables for runs #1-4) while increasing the selectivity towards hydrogenation and away from hydrocracking as shown on Fig. 3. The NH₃ effect is less than first order in NH₃, i.e. increasing quantities of NH₃ have progressively lesser effects. These observations are consistent with the generalization that catalyst acidity accelerates hydrocracking and that NH₃ acts to neutralize acid sites.

Similar analyses of data at 330°C and 300°C yield information on the effect of temperature on selectivity. Fig. 4, utilizing run #9 at 13.3 kPa and 300°C, shows that selectivity is markedly increased at lower temperatures. This is consistent with a broad generalization that activation energies for hydrogenation reactions are typically substantially less than for hydrocracking reactions. The activation energy for the overall reaction at 13.3 kPa is about 60 kJ, as shown on Figure 5.

Summary

For the model reaction studied, the addition of NH₃ increases the selectivity towards ring hydrogenation (generally desired) and away from dealkylation (generally undesired). However the overall reaction rate for a fixed temperature drops substantially. Selectivity is the greatest at the lowest temperatures. The effect of NH₃ is less than proportional to its partial pressure. The results obtained here suggest how operating conditions might be adjusted to obtain an optimum amongst desired reaction rates, conversion and selectivity, in the presence of small concentrations of NH₃ or other bases.

Experimental work and data analysis on this grant have now been completed. The final report, to be completed in the next month or two, will summarize all the studies under this grant and present them in the broader context of how a variety of catalytic hydrotreating reactions may be controlled with ammonia.

APPENDIX

Run # 5

FIGURE 1

RUN #5

Determination of k_1 and k_2

FIGURE 2

Selectivity vs PNH₃

$T=360^{\circ}\text{C}$

FIGURE 3

Selectivity vs Temperature

FIGURE 4

Activation Energy

FIGURE 5

RUN # 1

T=360 °C P_{tot}= 6.9 MPa; P_{PBz}=24.4 kPa; P_{NH3}=0 kPa

P_{H2S}=13.3 kPa

Carrier : n-Hexadecane (934.6 ml)
PBz : 0.24 mol/liter (=33.41 ml)
Propylamine : 0.133mol/liter (=0 ml)
1-Dodecanethiol : 0.133 mol/liter (=31 ml)

Space time T	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

$$k_1 + k_2 = 13.2 \cdot 10^{-4}$$

$$k_1 = 11.22 \cdot 10^{-4}$$

$$k_2 = 1.98 \cdot 10^{-4}$$

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 : 0.133 mol/liter (=10.91 ml)
1-Dodecanethiol : 0.133 mol/liter (=31 ml)

Space time T	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

$$k_1 + k_2 = 1.7 \cdot 10^{-4}$$

$$k_1 = 1.547 \cdot 10^{-4}$$

$$k_2 = 0.153 \cdot 10^{-4}$$

RUN # 3

T=360 °C P_{tot}= 6.9 MPa; P_{PBz}=24.4 kPa; P_{NH3}=24.4 kPa

P_{H2S}=13.3 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 T	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

$$k_1 + k_2 = 1.4 \cdot 10^{-4}$$

$$k_1/k_2 = \frac{1.302 \cdot 10^{-4}}{0.098 \cdot 10^{-4}}$$

RUN # 4

T=360 °C P_{tot}= 6.9 MPa; P_{PBz}=24.4 kPa; P_{NH3}=48.8 kPa

P_{H2S}=13.3 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 T	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

$$k_1 + k_2 = 1.3 \cdot 10^{-4}$$

$$k_1 = 1.22 \cdot 10^{-4}$$

$$k_2 = 0.078 \cdot 10^{-4}$$

RUN # 5

T=330 °C P_{tot}= 6.9 MPa; P_{PBz}=24.4 kPa; P_{NH3}= 0 kPa

P_{H2S}=13.3 kPa

Carrier : n-Hexadecane (934.6 ml)
PBz : 0.24 mol/liter (=33.41 ml)
Propylamine : 0.133mol/liter (=0 ml)
1-Dodecanethiol : 0.133 mol/liter (=31 ml)

Space time T	C _A /C _{A0}	C _B /C _{A0}	C _D /C _{A0}
50	0.980	0.0165	0.0022
100	0.961	0.0330	0.0040
200	0.930	0.064	0.0087
400	0.860	0.120	0.0160
600	0.790	0.179	0.0250

$$k_1 + k_2 = 3.8 \cdot 10^{-4}$$

$$k_1 = 3.324 \cdot 10^{-4}$$

$$k_2 = 0.463 \cdot 10^{-4}$$

RUN # 6

T=330 °C P_{tot}= 6.9 MPa; P_{PBz}=24.4 kPa; P_{NH3}=13.3 kPa

P_{H2S}=13.3 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 T	C _A /C _{A0}	C _B /C _{A0}	C _D /C _{A0}
50	0.994	0.00452	0.00035
100	0.982	0.00925	0.00068
200	0.980	0.0210	0.0013
400	0.960	0.0366	0.0028
600	0.941	0.0521	0.0041

$$k_1 + k_2 = 1 \cdot 10^{-4}$$

$$k_1 = 0.93 \cdot 10^{-4}$$

$$k_2 = 0.07 \cdot 10^{-4}$$

RUN # 7

$T=330^{\circ}\text{C}$ $P_{\text{tot}}=6.9\text{ MPa}$; $P_{\text{PBz}}=24.4\text{ kPa}$; $P_{\text{NH}_3}=24.4\text{ kPa}$

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

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 T	C_A/C_{A0}	C_B/C_{A0}	C_D/C_{A0}
50	0.995	0.00192	0.00001
100	0.994	0.00380	0.00019
200	0.991	0.00764	0.00039
400	0.983	0.0151	0.00079
600	0.972	0.0226	0.00110

$$k_1 + k_2 = 0.4 \cdot 10^{-4}$$

$$k_1 = 0.38 \cdot 10^{-4}$$

$$k_2 = 0.02 \cdot 10^{-4}$$

RUN # 8

T=330 °C P_{tot}= 6.9 MPa; P_{PBz}=24.4 kPa; P_{NH3}=48.8 kPa

P_{H2S}=13.3 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 T	C _A /C _{A0}	C _B /C _{A0}	C _D /C _{A0}
50	0.999	0.00096	0.00004
100	0.998	0.00190	0.00008
200	0.996	0.00380	0.00015
400	0.992	0.00764	0.00031
600	0.988	0.01140	0.00048

$$k_1 + k_2 = 0.2 \cdot 10^{-4}$$

$$k_1 = 0.192 \cdot 10^{-4}$$

$$k_2 = 0.008 \cdot 10^{-4}$$

RUN # 9

$T=300^{\circ}\text{C}$ $P_{\text{tot}}= 6.9 \text{ MPa};$ $P_{\text{PBz}}=24.4 \text{ kPa};$ $P_{\text{NH}_3}=13.3 \text{ kPa}$

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

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

Space time T	C_A/C_{A0}	C_B/C_{A0}	C_D/C_{A0}
50	0.997	0.00235	0.000122
100	0.995	0.00472	0.000245
200	0.980	0.00940	0.000492
400	0.970	0.01870	0.000980
600	0.960	0.02700	0.001470

$$k_1 + k_2 = 0.500 \cdot 10^{-4}$$

$$k_1 = 0.475 \cdot 10^{-4}$$

$$k_2 = 0.025 \cdot 10^{-4}$$

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