

Article

# Investigating the Effects of Organonitrogen Types on Hydrodearomatization Reactions over Commercial NiMoS Catalyst

## Supplementary information

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### 1. Equilibrium constants

As mentioned in the main text, there were a few reactions that could be under thermodynamic control. Herein, the available equilibrium constants are presented. The equilibrium constant presented here is not the true equilibrium constant but a modified one, i.e.,

$$K'_i = K_i \cdot p_{H_2} \quad (S1)$$

#### 1.1 Phenanthrene hydrogenation

First off, the phenanthrene hydrogenation reactions where could be of interest of thermodynamic control is the first hydrogen step to DIPHE or TETPHE, i.e., reaction 1 and 2. See Figure 1 in the main paper.

Based on the work by Frye [1], equilibrium constants for the reactions were experimentally determined. The current reactor system was operated at 120 barg and results in a hydrogen partial pressure of about 106 bar. Using this for the reactions 1 and 2, the modified equilibrium constants at the tested reactor temperature are presented in Table S1.

**Table S1** Modified equilibrium constants for the phenanthrene hydrogenation reaction 1 and 2, as seen in Figure 1.

Reactor temperature [°C]	K' <sub>1</sub>	K' <sub>2</sub>
280	4.1	466
300	2.8	179.8
320	2.0	73.9

As can be seen, the constant for reaction 1 is very small and indicates that one cannot assume that the reaction is irreversible at the tested temperatures even at a hydrogen partial pressure of 106 bar. However, the second reaction can most likely be assumed to be irreversible for all practical purposes.

#### 1.2 Hydrogenation of carbazole

In addition to phenanthrene, there are several hydrogenation steps in the HDN of carbazole, its HDN network is shown in Figure 7 in the main paper. Steele and Chirico [2] estimated the equilibrium constants for the HDN of carbazole. Based on that data, the modified equilibrium constant at the hydrogen partial pressure of 106 bar is presented in table S2 for the first two hydrogenation steps for carbazole, i.e., CBZ:4H-CBZ:6H-CBZ.

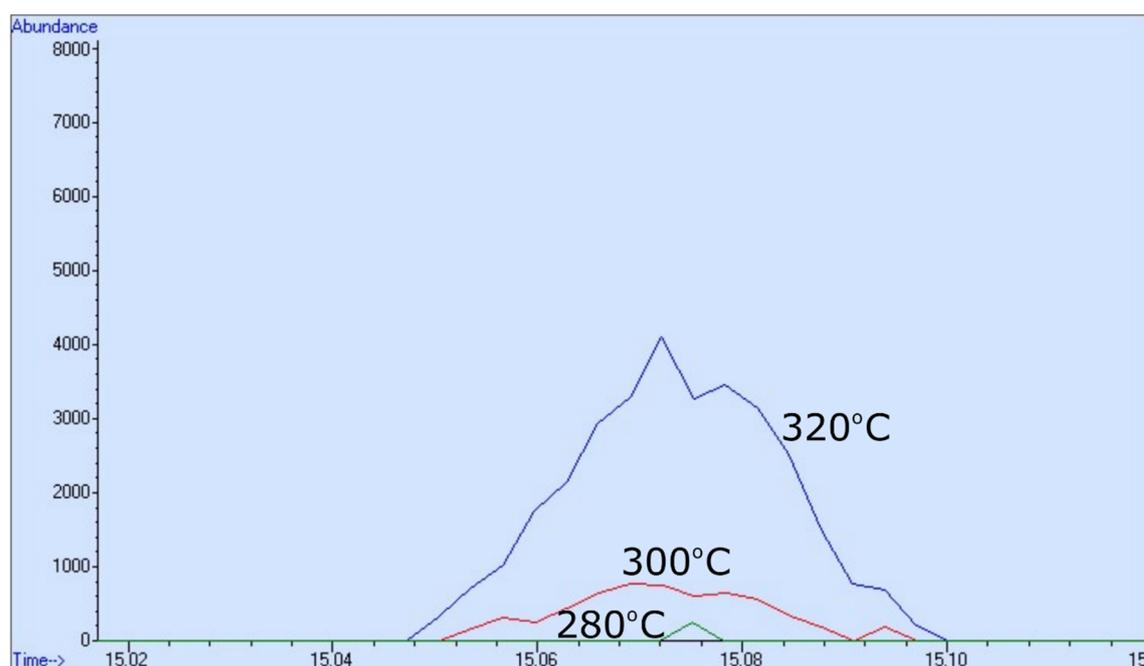
**Table S2.** Modified equilibrium constants for the two first hydrogenation steps for carbazole HDN, figure 7.

Reactor temperature [°C]	K' <sub>CBZ-4HCBZ</sub>	K' <sub>4HCBZ-6HCBZ</sub>
280	61	0.05
300	26	0.04
320	12	0.04

Based on those numbers, it can be seen that the modified equilibrium constant of 4H-CBZ to 6H-CBZ is very small, indicating that 4H-CBZ is the most thermodynamically favored product.

## 2. GC-MS of acridine experiments

As stated in the main text, even though the extent of HDN was generally low for acridine, some of its HDN products were detected in small quantities. In **Figure S1** and **Figure S2**, the chromatogram for the ion mass 180 as well as the ion spectrum for that is shown. 180 is the qualifier ion mass for the acridine HDN product DCHM. The reactor temperature is varied and it can be seen that the abundance of 180 increases with reactor temperature. Additionally, the ion peak of 180 is not detected when acridine was not present in the reactant feed. This indicates that trace amounts of HDN does occur, even at the lowest reactor temperature of 280 °C.



**Figure S1.** Chromatogram for the 180 m/z in the liquid product when acridine was present in the reactant feed. 180 is the qualifying ion for DCHM.

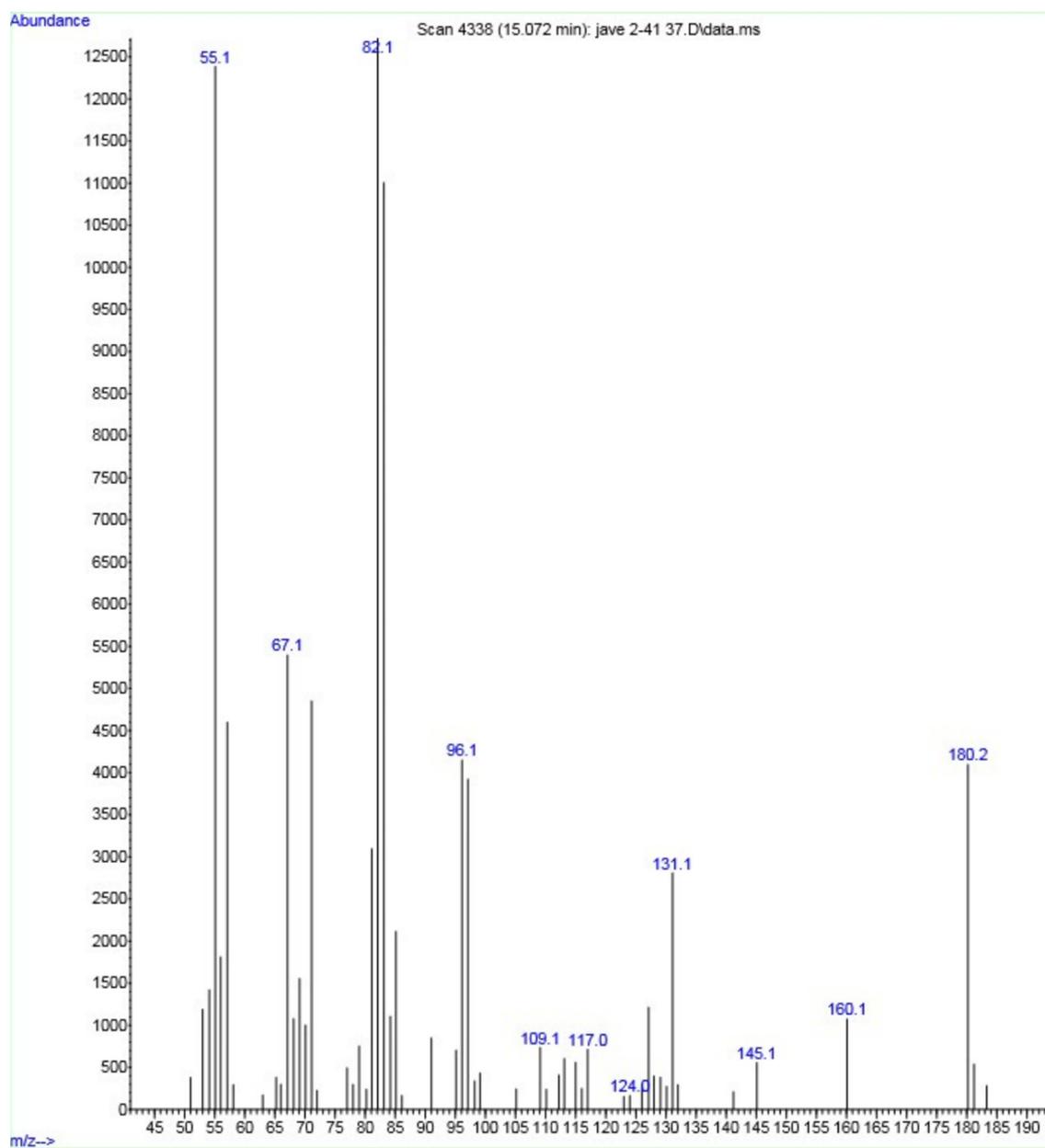


Figure S2. Ion spectrum for the peak containing 180 m/z, from the experiment with a reactor temperature of 320 °C and acridine is in the reactant feed.

## References

1. Frye, C.G. Equilibria in the hydrogenation of polycyclic aromatics. *J. Chem. Eng. Data* **1962**, *7*, 592–595.
2. Steele, W.V.; Chirico, R.D. *Thermodynamics of the Hydrodenitrogenation of Carbazole*; National Institute for Petroleum and Energy Research: Bartlesville, OK, USA, 1991; 43p.