Tetralin Hydrogenation over Supported Nickel Catalysts

Supporting Information

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S1 *Temperature Programmed Reduction (TGA-TPR) of fresh calcined support and meatal precursor:*

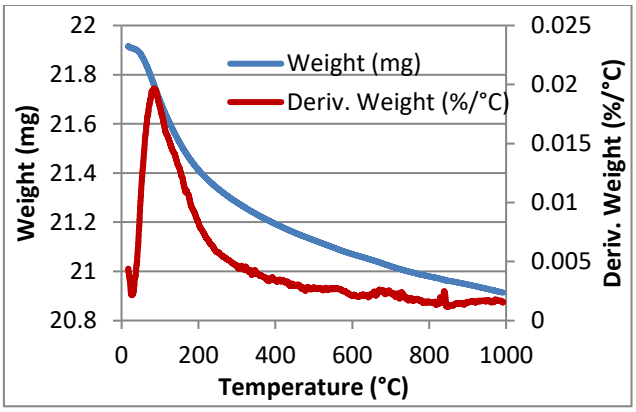


Figure S1: TGA-TPR and DTG profiles for calcined unloaded alumina support.

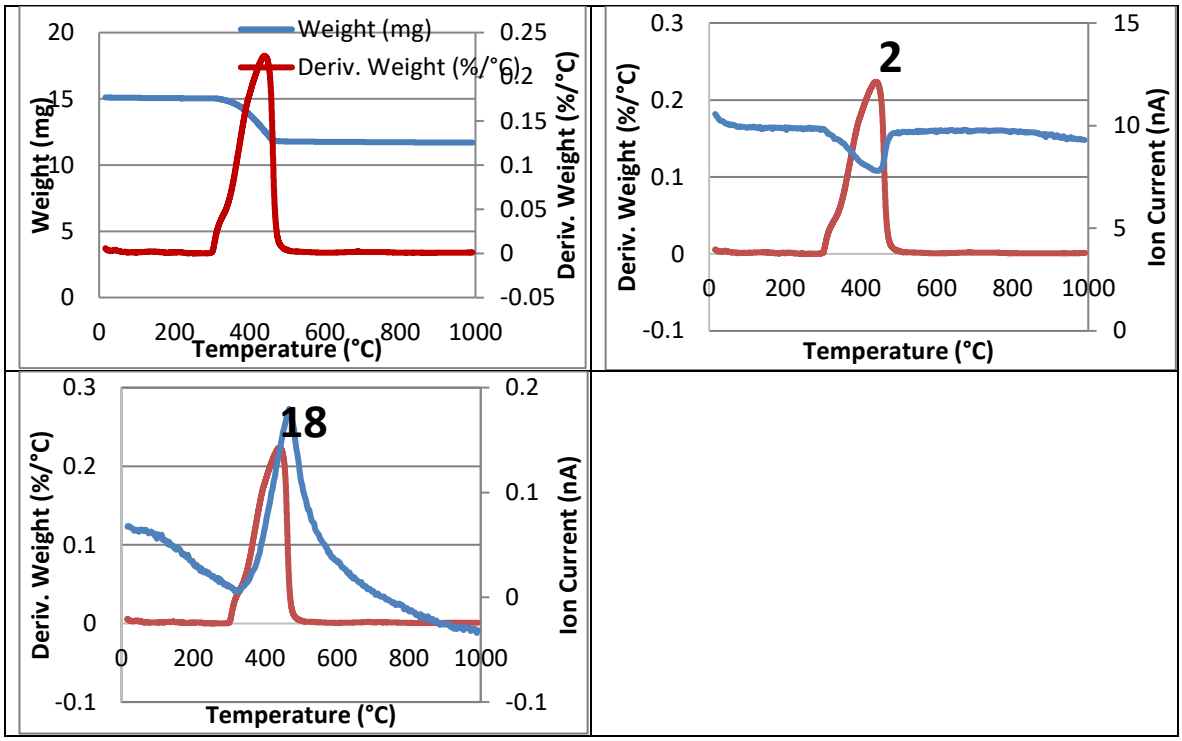
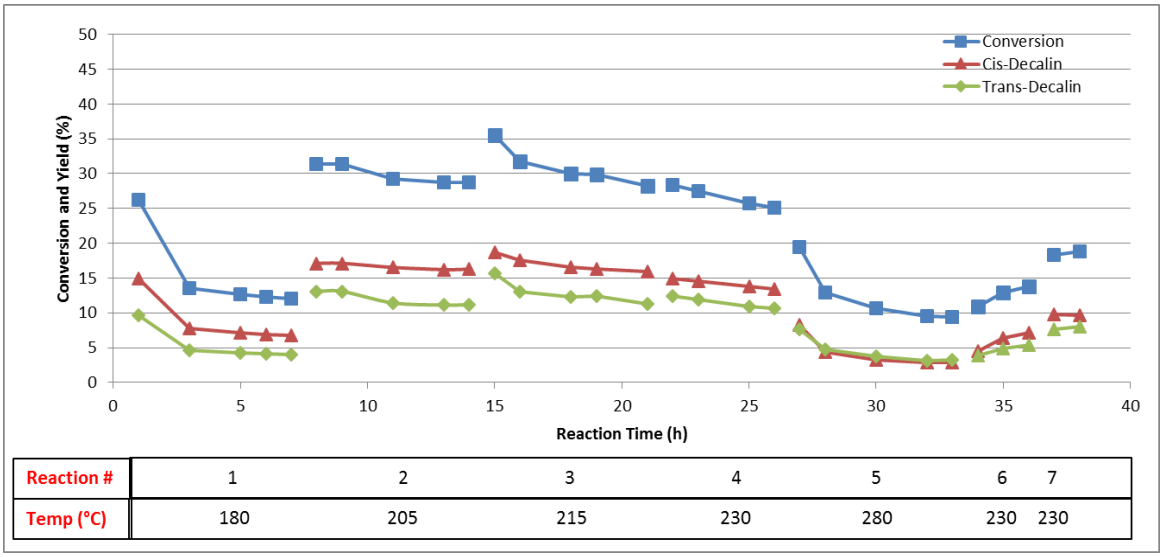


Figure S2: TGA-TPR and DTG profiles together with mass spectra of the evolved gases for calcined nickel precursor.

S2 *Optimization of the Reaction Operating Conditions:*

A series of tests were conducted on HDC2 catalyst to study the impact of changing the conditions on the conversion and selectivity of tetralin hydrogenation reaction. Several reaction parameters were tested in this investigation such as temperature, pressure, and hydrogen/hydrocarbon (H_2/HC) ratio. Temperature optimisation study was performed to evaluate the effect of increasing temperature which ranged from 180 to 280 °C without changing the catalyst (**Figure S3**). The catalyst was first loaded to the reactor and reduced in-situ as described in **section 2.3**. The reactor was operated at fixed pressure and hydrogen flow rate (i.e 5 barg and 140 ml/min H_2) while varying the temperature. Each test was conducted for 2-7 h and then the hydrocarbon feed was stopped overnight followed by adjusting the reactor to a higher or lower temperature. It is important to note that after the fifth reaction, the reactor (including heater, pump, and mass flow controller) was turned off without depressurising it. After two days, it was turned back on to test the catalyst at lower temperature (230 °C) for 3 h and then kept at that temperature overnight while the hydrocarbon feed was off to prepare it for the next reaction. In general, the acquired GC results suggested that increasing the temperature increased the activity steadily to reach its maximum around tetralin boiling point (i.e. at 207 °C) and then it started to decrease as the reaction proceeded to higher temperatures. Increasing the temperature also influenced trans/cis ratio where the cumulative ratios were 0.6, 0.7, 0.75, 0.8, and 1 at 180, 205, 215, 230, and 280 °C respectively. Similarly, naphthalene yield increased from 0.03 to 3% which raised the selectivity from 0.3% to 27% at 180 and 280 °C. In terms of octalins, higher selectivity was recorded at 180 °C which was reduced when the temperature was increased to 205 °C and then remained relatively constant at higher temperatures. During each reaction, the selectivity for cis-decalin and octalins was increasing every hour as the catalyst was deactivating while trans-decalin was decreasing. Naphthalene selectivity on the other hand remained almost constant at all temperatures except 280 °C where

all products were decreasing and naphthalene was increasing. Moreover, the results showed quick deactivation during the first hour of the reactions conducted at 180 and 280 °C. At 180 °C, the deactivation could be due to loss of some active site or blocking small pore structure of the catalyst. On the other hand, the deactivation at 280 °C could be due to carbonaceous material laydown since activity was not recovered when the temperature was reduced to 230 °C. Keeping the reaction at that temperature (i.e. 230 °C) overnight slightly restored the activity of the catalyst as presented in the last reaction. Thermodynamic theoretical calculations were in good agreement with the activity results but not with the isomer ratio results. The calculation of the equilibrium constant using Gibbs free energies indicated that tetralin hydrogenation undergoes spontaneous reaction to form decalins at temperatures below 227 °C. Once at that temperature, the reverse reaction starts to become more significant such that both decalins and tetralin begin to dehydrogenate. The reaction completely shifts to dehydrogenation within one hundred degrees (*i.e*. by 327 °C). These findings agreed with several approaches that were reported in the literature [27-29] which tackled thermodynamic aspects of naphthalene and tetralin based on Frye and co-workers experimental data [30-31]. These literatures stated that complete saturation of both naphthalene and tetralin is impossible above 327 °C due to thermodynamic limitation and that the decrease in the conversion with temperature is related to the exothermic nature of tetralin hydrogenation that favoured low reaction temperature. Moreover, it can be inferred from our study and other studies [3,32-34] that the drop in conversion while increasing temperature could be related to the balance between tetralin hydrogenation and dehydrogenation.



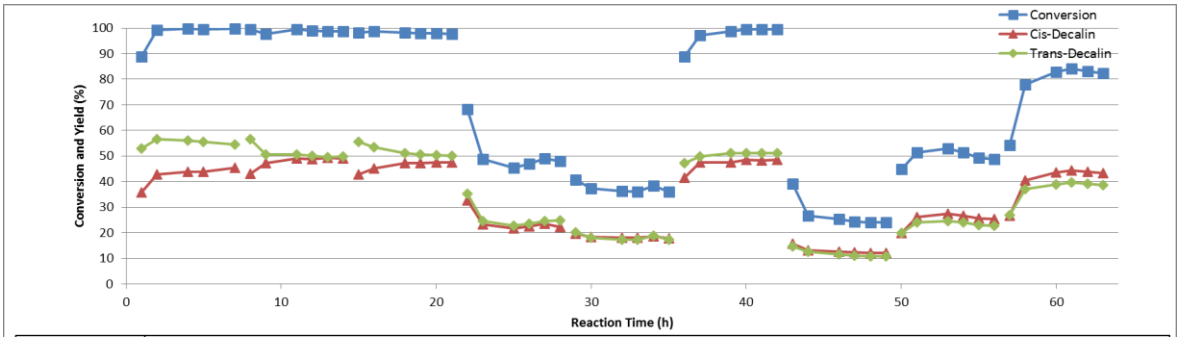
Reaction #	1	2	3	4	5	6	7
Temp (°C)	180	205	215	230	280	230	230

Cumulative products yield at the end of each reaction (%)							
Reaction #	1	2	3	4	5	6	7
1,9-Octalin	0.1065	0.1271	0.1218	0.1138	0.0648	0.0951	0.1114
9,10-Octalin	1.0913	1.0745	0.9250	0.7457	0.2815	0.6396	0.7455
Naphthalene	0	0.0398	0.0557	0.1782	3.2706	0.8739	0.2530

Figure S3: Tetralin conversion and decalins yields for HDC2 catalyst under 5 barg, 4.3 H_2/HC ratio, and different temperatures

The next tests were carried out to study the influence of changing hydrogen pressure and hydrogen to hydrocarbon feed molar ratio (H_2/HC) on the reactivity and selectivity of the catalyst. It is important to mention that H_2/HC was altered by means of changing the hydrogen flow rate in order to maintain the same WHSV and LHSV for all the reactions. The same procedures were implemented as the previous test where HDC2 catalyst was tested for 7 hours, while fixing two parameters and varying the third. Nine reactions were conducted in sequence without changing the catalyst as presented in **Figure S4**. The catalyst was tested at three different pressures (5, 10, and 15 barg) and three different H_2/HC ratio (4.3, 7.5, and 10.5). The evaluation was first conducted at high H_2/HC ratio while decreasing the pressure then at low H_2/HC ratio while increasing the pressure and that the reaction conditions of the first test was repeated in between. The results revealed that the activity was proportional to both hydrogen pressure and H_2/HC ratio. As for product selectivity, the reaction data indicated that increasing

H_2/HC ratio increased the selectivity toward trans-decalin regardless of the reaction pressure. In contrast, increasing the pressure increased the selectivity toward *trans*-decalin at high H_2/HC ratio while the selectivity of *cis*-decalin was increased when the pressure was increased at low H_2/HC. In this regards, additional experiments were conducted on different catalysts prepared with different techniques and loadings for 7h (fresh catalyst each run) to further investigate the effects of hydrogen pressure and H_2/HC ratio on the selectivity. The attained findings from these experiments agreed with the result presented in **Figure S4** in terms of increasing H_2/HC ratio where both activity and *trans*-decalin selectivity were enhanced. However, the influence of increasing the pressure varied when different catalysts were tested at the same conditions. *Trans*-decalin selectivity was improved when the pressure was increased on 5% HDC catalyst while 2.5% IMP catalyst enhanced the selectivity of *cis*-decalin when the pressure was increased. This explains the earlier findings of the pressure effects (**Figure S4**). It indicated that the catalyst was active in the first few runs that decayed with time as observed in reaction #6 (same conditions as the first run) and resulted in changing the physical properties of the catalyst which in turn affected the selectivity of the later runs. Thus, it can be inferred from these findings that the selectivity was influenced by the physical properties of these catalysts such as population, location, and particle size of the active metal. The results revealed that 100% conversion was achieved at 10 barg, 230 °C, and 10.5 H_2/HC ratio.

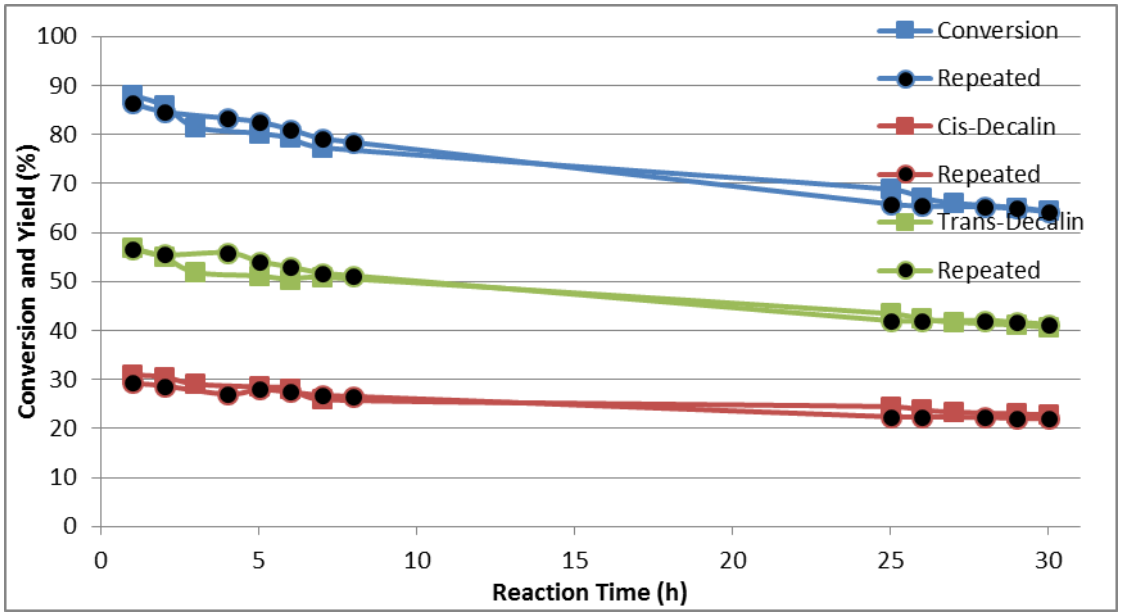


Reaction #	1	2	3	4	5	6	7	8	9
Pressure (bar)	15	15	10	5	5	15	5	10	15
H_2/HC ratio	10.5	7.5	10.5	10.5	7.5	10.5	4.3	4.3	4.3

Cumulative products yield at the end of each reaction (%)									
Reaction #	1	2	3	4	5	6	7	8	9
1,9-Octalin	0	0	0	0.1011	0.1075	0	0.1132	0.0999	0.0453
9,10-Octalin	0	0	0	0.5462	0.6027	0	0.6327	0.5829	0.2484
Naphthalene	0	0	0	0.1888	0.2215	0	0.3480	0.2199	0.0344

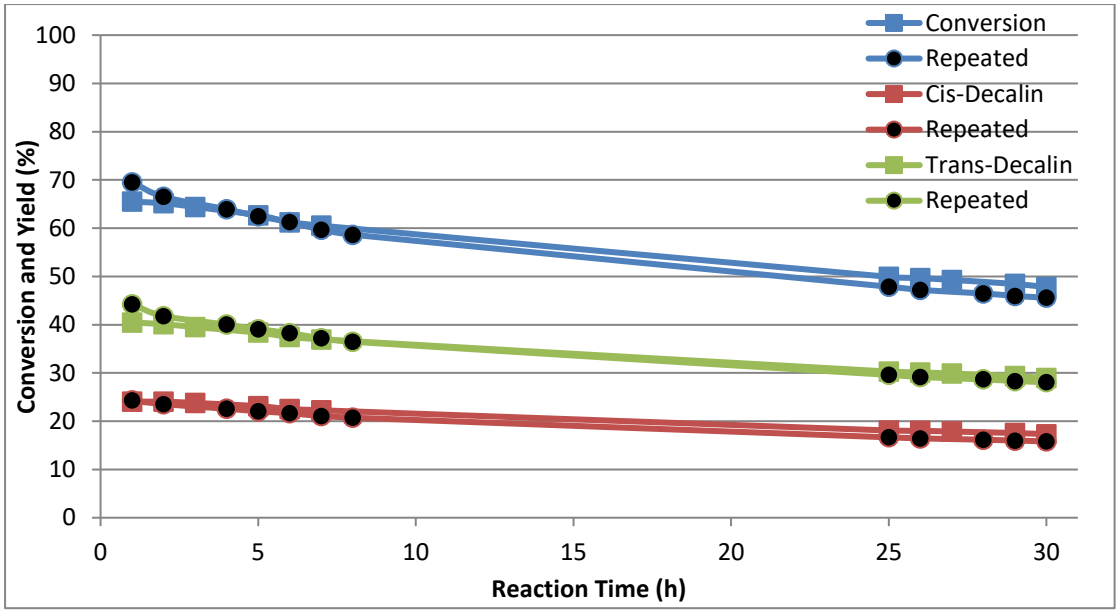
Figure S4: Tetralin conversion and decalins yields for HDC2 catalyst at 230 °C and different hydrogen pressure and H_2/HC ratio.

S3 Reproducibility of the evaluation results:



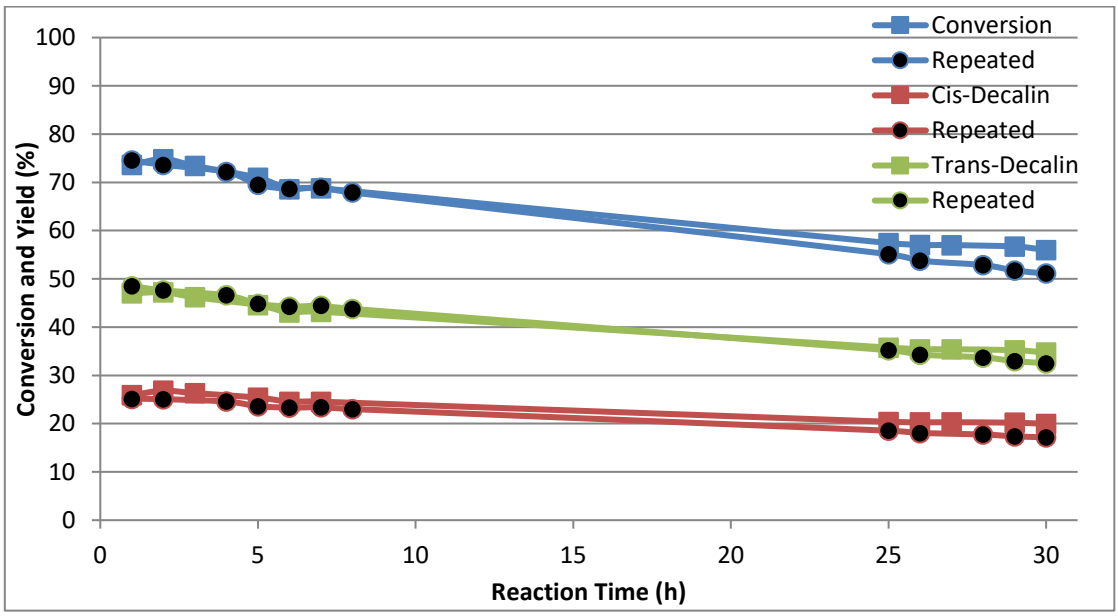
Cumulative products yield at the end of each reaction (%)		
1,9-Octalin	9,10-Octalin	Naphthalene
0.0677	0.7358	0

Figure S5: Tetralin conversion and decalins yields for IMP1 catalyst under 5 barg, 210 °C, and 7.5 H_2/HC ratio for 30 hours together with repeated reaction.



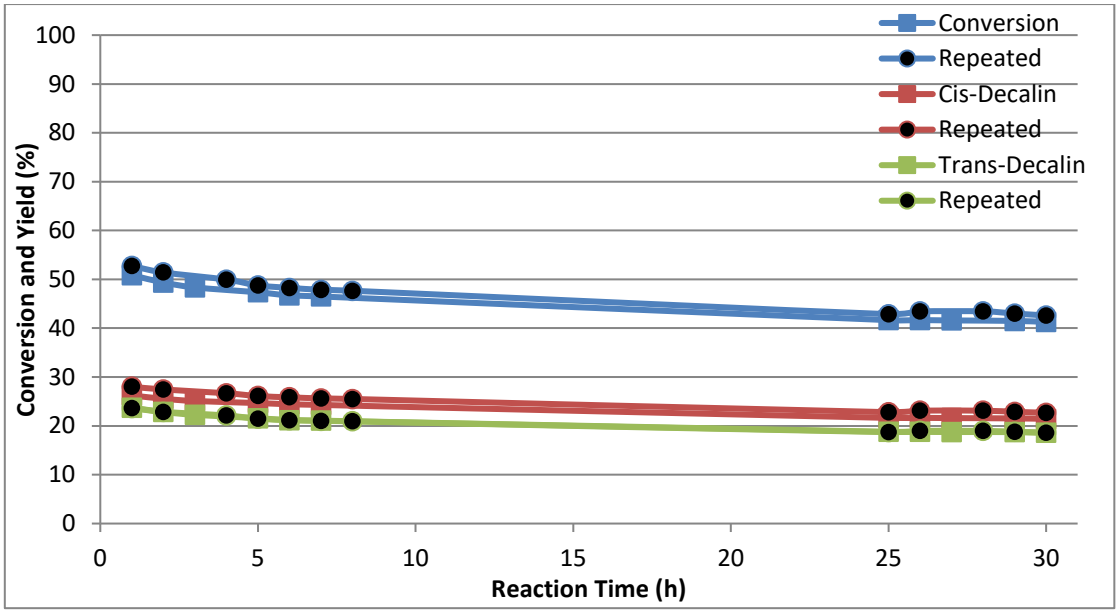
Cumulative products yield at the end of each reaction (%)		
1,9-Octalin	9,10-Octalin	Naphthalene
0.1432	1.2763	0

Figure S6: Tetralin conversion and decalins yields for PD1 catalyst under 5 barg, 210 °C, and 7.5 H_2/HC ratio for 30 hours together with repeated reaction.



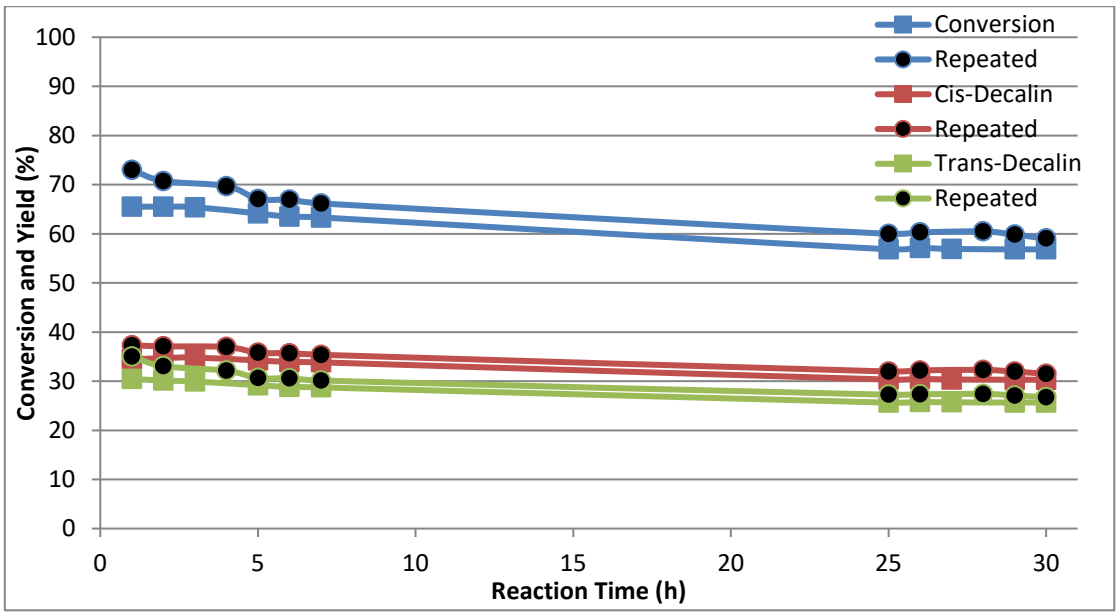
Cumulative products yield at the end of each reaction (%)		
1,9-Octalin	9,10-Octalin	Naphthalene
0.1176	1.0616	0

Figure S7: Tetralin conversion and decalins yields for HDC1 catalyst under 5 barg, 210 °C, and 7.5 H_2/HC ratio for 30 hours together with repeated reaction.



Cumulative products yield at the end of each reaction (%)		
1,9-Octalin	9,10-Octalin	Naphthalene
0.1234	1.057	0

Figure S8: Tetralin conversion and decalins yields for PD2 catalyst under 5 barg, 210 °C, and 7.5 H_2/HC ratio for 30 hours together with repeated reaction.



Cumulative products yield at the end of each reaction (%)		
1,9-Octalin	9,10-Octalin	Naphthalene
0.0905	0.7391	0

Figure S9: Tetralin conversion and decalins yields for HDC2 catalyst under 5 barg, 210 °C, and 7.5 H_2/HC ratio for 30 hours together with repeated reaction.

S4 Catalyst Post-Reaction Characterization:

TPOs of the catalysts post reaction were obtained using the TGA-MS. The weight loss profiles are shown below.

Table S1: TPO - weight loss (between 250-700 °C) of the spent nickel catalysts synthesised with different methodologies and metal precursors and evaluated at 5 barg, 210 °C, and 7.5 H_2/HC ratio for 30 hours.

Sample	Sample description	TPO Weight loss (wt.%)
Al_2O_3	Unloaded Alumina	5.80
IMP1	5% Ni/Al_2O_3 (Nickel Nitrate - Impregnation)	1.23
PD1	5% Ni/Al_2O_3 (Nickel Nitrate - Precipitation-Deposition)	1.74
HDC1	5% Ni/Al_2O_3 (Nickel Nitrate - HDC)	1.43
PD2	5% Ni/Al_2O_3 (Nickel Carbonate - Precipitation-Deposition)	1.71
HDC2	5% Ni/Al_2O_3 (Nickel Carbonate - HDC)	1.75

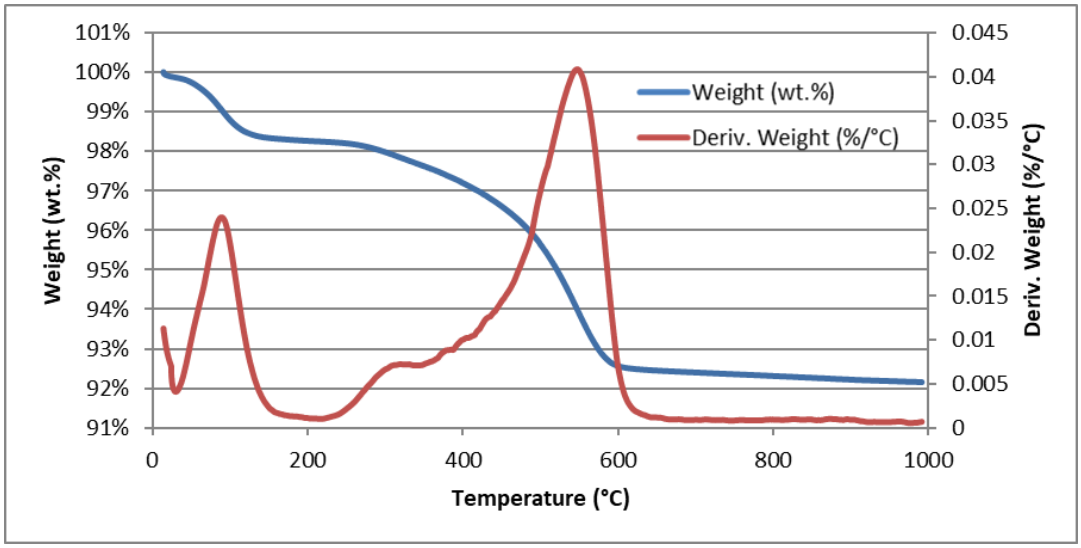


Figure S10: TGA-TPO and DTG profiles for spent Alumina support evaluated at 5 barg, 210 °C, and 7.5 H_2/HC ratio for 30 hours.

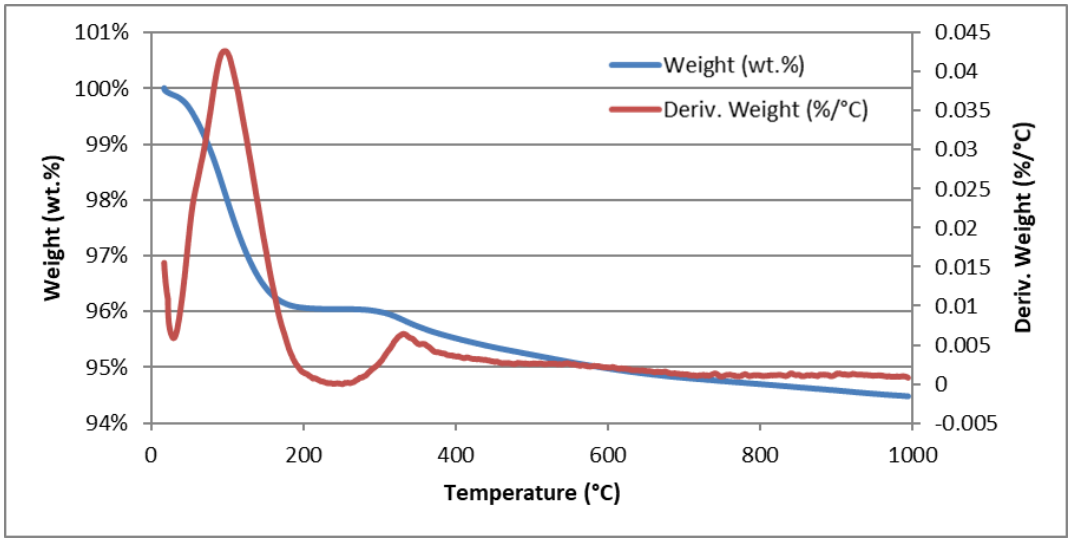


Figure S11: TGA-TPO and DTG profiles for spent IMP1 catalyst evaluated at 5 barg, 210 °C, and 7.5 H_2/HC ratio for 30 hours.

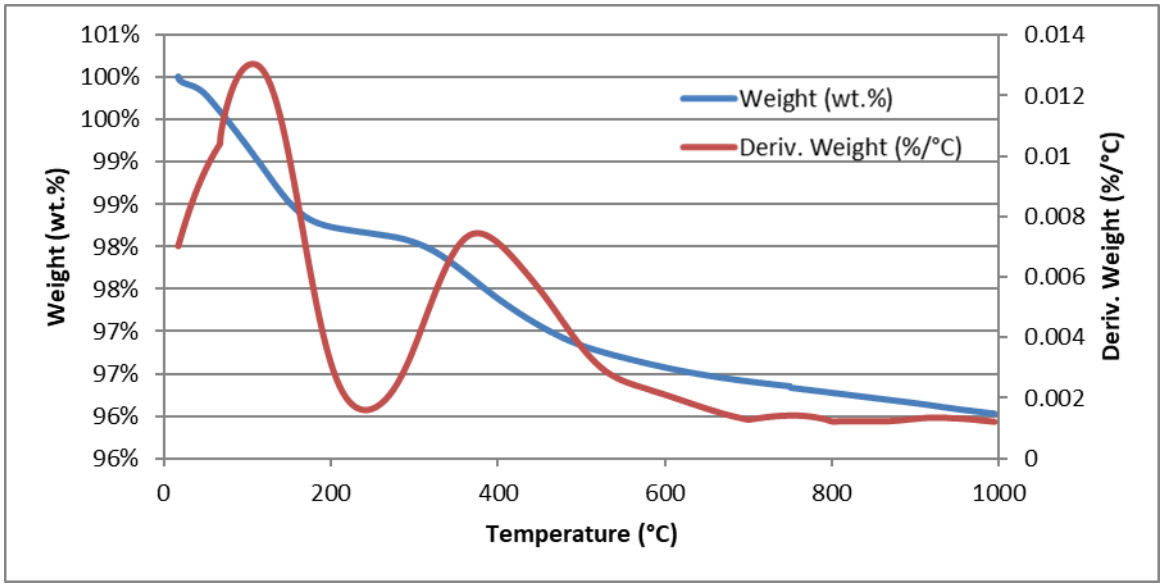


Figure S12: TGA-TPO and DTG profiles for spent PD1 catalyst evaluated at 5 barg, 210 °C, and 7.5 H_2/HC ratio for 30 hours.

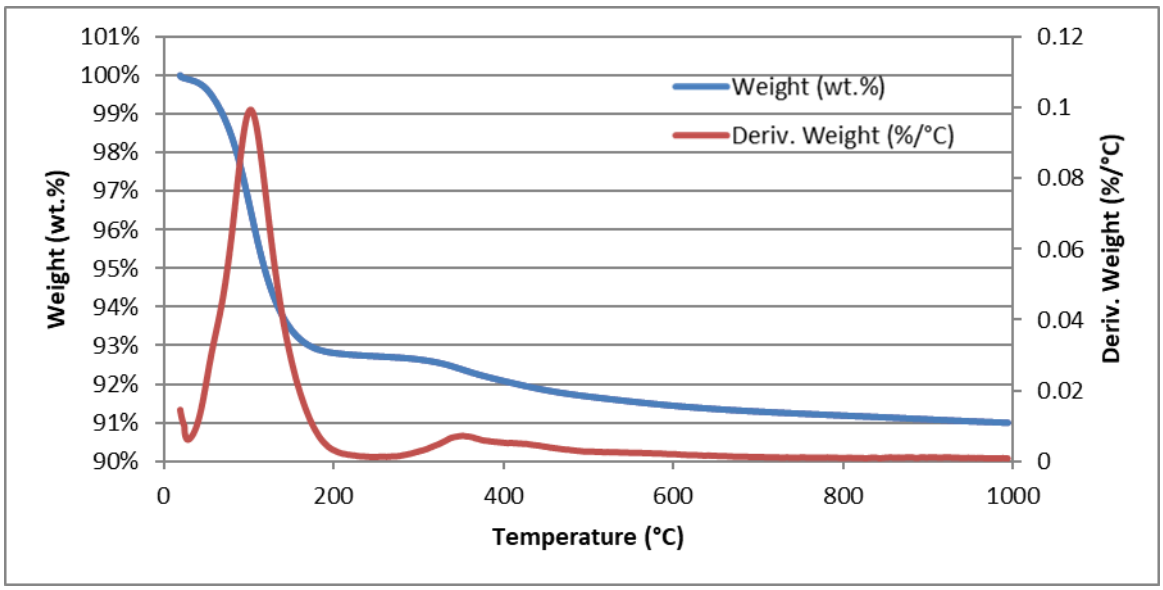


Figure S13: TGA-TPO and DTG profiles for spent HDC1 catalyst evaluated at 5 barg, 210 °C, and 7.5 H_2/HC ratio for 30 hours.

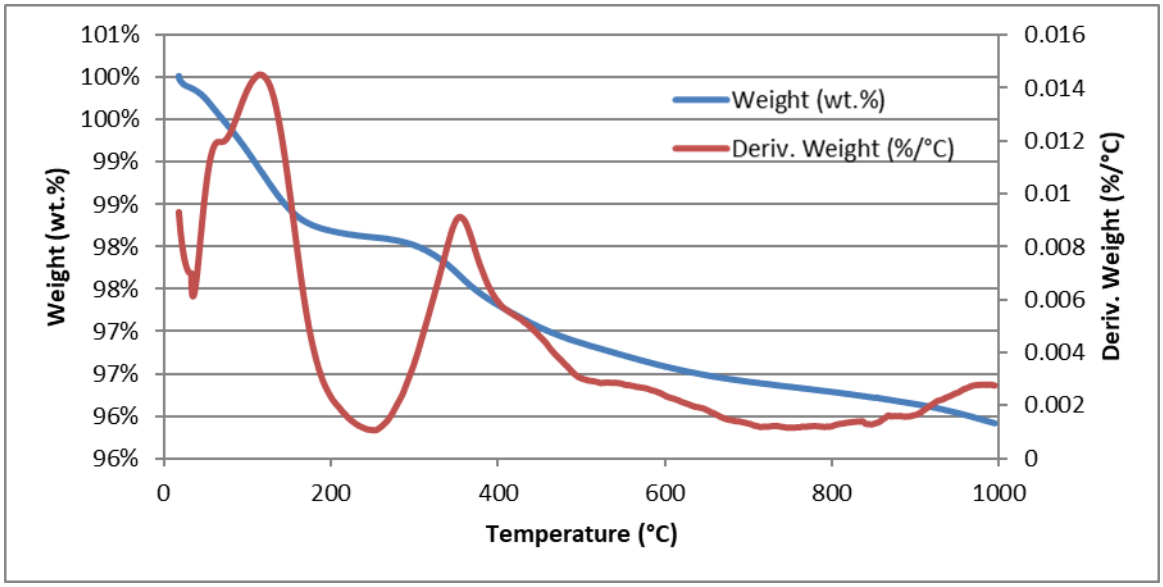


Figure S14: TGA-TPO and DTG profiles for spent PD2 catalyst evaluated at 5 barg, 210 °C, and 7.5 H_2/HC ratio for 30 hours.

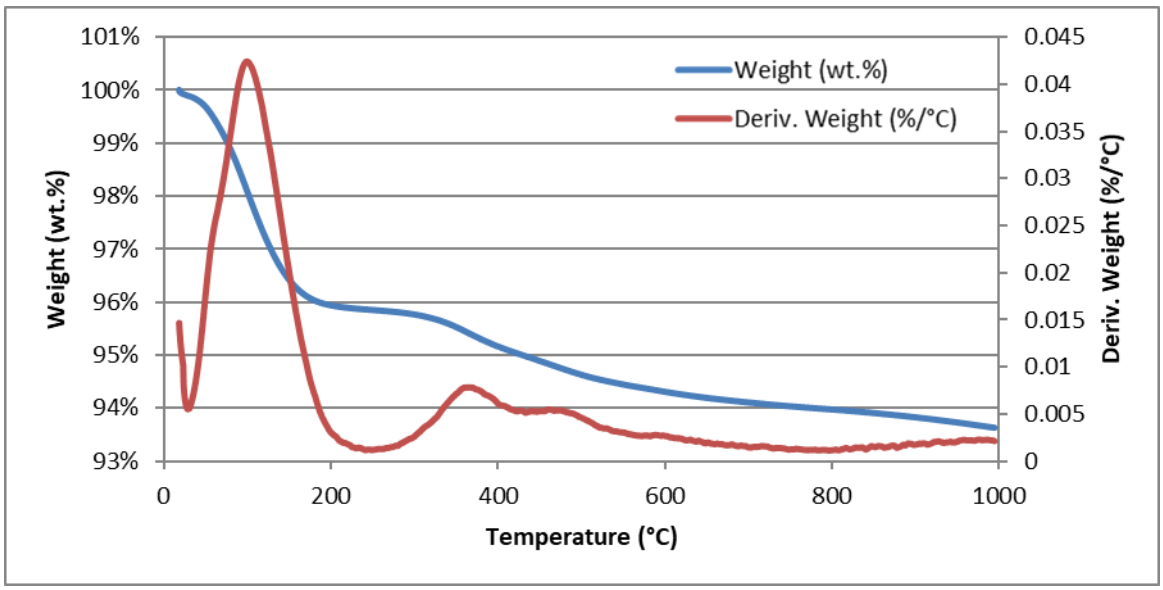


Figure S15: TGA-TPO and DTG profiles for spent HDC2 catalyst evaluated at 5 barg, 210 °C, and 7.5 H_2/HC ratio for 30 hours.