

Hydrodeoxygenation and hydrodenitrogenation of
n-hexadecanamide with supported NiMo sulfide
catalysts - Supporting Information

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A Details on ICP-OES analysis

Prior to ICP-OES analysis, samples were digested in aqua regia for 60 min at 200 °C in aqua regia (7.5 ml HCl, 2.5 ml HNO₃). The obtained solutions were filtered, diluted with MilliQ water and analyzed. The ICP-OES analysis was performed using an Agilent 5900 SVDV ICP-OES spectrometer. An Agilent Seaspray borosilicate glass nebulizer was used for liquid sample introduction, together with a borosilicate glass spray chamber and an ICP quartz torch intended for analysis of aqueous samples. The plasma was analyzed in synchronous vertical dual view (SVDV) mode. Scandium (line at 361.383 nm) was used as an internal standard. Three replicate measurements were collected per sample injection, and the results of these replicates were averaged. Two blank 5% HNO₃ samples were analyzed between each sample, in order to ensure no sample to sample carryover occurred.

B Details on the XPS analysis

The atomic (molar) percentage of each element on the surface analyzed was determined by comparing the intensities of the peaks associated with each detected element, and applying the appropriate atomic sensitivity factors. Thus, Equation 1 was obtained.

$$[i] = \frac{\frac{I_i}{A_i}}{\sum_{j=1}^N \left(\frac{I_j}{A_j} \right)} \quad (1)$$

where $[i]$ is the atomic (molar) percentage of element i , I_i the intensity of the peak(s) associated element i and A_i the atomic sensitivity factor of i .

The Mo 3d spectra was deconvoluted into several standard Gaussian-Lorentzian peaks, split due to spin-orbit splitting into doublet peaks with an inter-peak energy difference of 3.15 eV and an expected area ratio of 2:3. Based on the literature, three such doublet peaks should be present, corresponding to Mo(VI), Mo(V) and Mo(IV) species [1–4]. These peaks were assumed to correspond to molybdenum sulfide species, molybdenum oxysulfide species and molybdenum oxide species respectively, based on peak assignments in literature [1, 2, 4, 5] Thus, the sulfidation degree as evaluated by XPS is given by

$$\text{MoS}_2/\text{Mo} = \frac{I_{\text{Mo(IV)}}}{I_{\text{Mo(IV)}} + I_{\text{Mo(V)}} + I_{\text{Mo(VI)}}} \quad (2)$$

where $I_{\text{Mo(IV)}}$ is the intensity of the Mo(IV) peak, $I_{\text{Mo(V)}}$ is the intensity of the Mo(V) peak and $I_{\text{Mo(VI)}}$ is the intensity of the Mo(VI) peak.

Three Gaussian-Lorentzian peaks were fitted to the data and attributed to NiS_x , NiMoS , and NiO_x species, respectively. For each main peak, satellite peaks with an energy difference of 6.7 eV and an area ratio of 1:4 as well as doublet peaks with an energy difference of 17.3 eV and a theoretically expected area ratio of 1:2 were also fitted. Once this fitting and peak assignment had been done, the relative amount of the mixed NiMoS phase is given by

$$\text{NiMoS}/\text{Ni} = 100\% \frac{I_{\text{NiMoS}}}{I_{\text{NiMoS}} + I_{\text{NiS}_x} + I_{\text{NiO}_x}} \quad (3)$$

where I_{NiMoS} is the intensity of the NiMoS peak at 853.8 eV, I_{NiS_x} is the intensity of the NiS_x peak at 852.9 eV and I_{NiO_x} is the intensity of the NiO_x peak at 856.2 eV.

C Details on the TEM analysis

The average stacking numbers and average slab lengths were calculated using the Equations below:

$$\overline{N} = \frac{\sum_{i=1}^k N_i}{k} \quad (4)$$

$$\overline{L} = \frac{\sum_{i=1}^k l_i}{k} \quad (5)$$

where $\overline{N}$ is the average stacking number, $\overline{L}$ is the average slab length, k is the total number of particles counted, N_i is the stacking number of stack i and l_i is the length of slab i .

The edge dispersion (defined as the fraction of Mo atoms present on the catalytically active edge sites), can then be calculated using Equation 6 [6, 7]:

$$\begin{aligned} f_{\text{Mo}} &= \frac{\sum_{i=1}^k (6(n_i - 1)N_i)}{\sum_{i=1}^k ((3n_i^2 - 3n_i + 1)N_i)} \\ &= \frac{\sum_{i=1}^k \left(6 \left(\left(\frac{l_i}{2d_{\text{Mo-Mo}}} + \frac{1}{2} \right) - 1 \right) N_i \right)}{\sum_{i=1}^k \left(\left(3 \left(\frac{l_i}{2d_{\text{Mo-Mo}}} + \frac{1}{2} \right)^2 - 3 \left(\frac{l_i}{2d_{\text{Mo-Mo}}} + \frac{1}{2} \right) + 1 \right) N_i \right)} \end{aligned} \quad (6)$$

where f_{Mo} is the edge dispersion, k is the total number of particles counted, n_i is the amount of Mo atoms per side in stack i , N_i is the stacking number of stack i , l_i is the length of stack i and $d_{\text{Mo-Mo}}$ is the Mo-Mo distance, commonly assumed to be 3.2 Å [6].

Standard error estimates for the average stacking numbers, average slab lengths

and the edge dispersions were estimated using Equation 7:

$$\sigma_{\bar{x}} = \frac{\sigma_x}{N} \quad (7)$$

in which $\sigma_{\bar{x}}$ is the standard error of the average of property x , σ_x is the sample standard deviation of x and N is the number of datapoints.

D Details on the reaction product analytics

The response factors used for GC-FID analysis in this work are shown in Table S1 below.

Table S1: GC-FID response factors. Estimated response factors were calculated using equation suggested by de Saint Laumer *et al.* [8]

Analyte	Response factor	Type	Supplier	Purity
C12 paraffin (ISTD)	1	Calibrated	Merck	>99%
C16 amine	0,956	Calibrated	Tokyo Chemical Industry	>95%
C16 amide	0,869	Calibrated	Tokyo Chemical Industry	>95%
C15 paraffin	1,006	Calibrated	Aldrich	>99%
C15 olefin	0,995	Estimated	-	-
C16 paraffin	1,007	Calibrated	Sigma Aldrich	>99%
C16 olefin	0,997	Estimated	-	-
C16 alcohol	0,927	Calibrated	Acros Organics	96 %
C32 amine	0,991	Estimated	-	-
C32 amide	0,943	Estimated	-	-
C16 nitrile	0,949	Estimated	-	-
C16 acid	0,604	Calibrated	Riedel de Haën	>98%
C14 paraffin	1,004	Estimated	-	-
C16 thiol	0,882	Estimated	-	-

The response factors and the internal standards were used to determine the molality of the products in the reaction mixture using Equation 8.

$$b_i = b_{IS} \frac{A_i R_i}{A_{IS} R_{IS}} \quad (8)$$

where b_i is the molality of the product i in mol/g, b_{IS} is the molality of the internal standard in mol/g, A_i is the GC-FID peak area of the product i , A_{IS} is the GC-FID peak area of the internal standard, $R_{f,i}$ is the response factor of product i and $R_{f,IS}$ is the response factor of the internal standard.

The conversion of hexadecanamide was calculated based on the GC-FID results using Equation 9:

$$X_{amide} = \frac{b_{amide,0} - b_{amide,1}}{b_{amide,0}} \cdot 100\% \quad (9)$$

where X_{amide} is the amide conversion, $b_{amide,1}$ is the molality of the amine model compound in the product mixture in mol/g and $b_{amide,0}$ is the molality of the amine model compound in the zero sample in mol/g.

The yields of the products were calculated as a carbon-based yield, as the stoichiometry of the reactions was unknown. The carbon-based yield was calculated using Equation 10:

$$Y_i = \frac{b_i}{b_{amide,0}} \frac{N_{C,i}}{N_{C,amide}} \quad (10)$$

where Y_i is the carbon-based yield of the product i , b_i is the molality of product i in mol/g, $b_{amide,0}$ is the molality of the amide model compound in the zero sample in mol/g, $N_{C,i}$ is the number of carbon atoms in product i and $N_{C,amide}$ is the number of carbon atoms in the amide model compound. However, it should be noted that

the C₁₅ products (pentadecane and related olefins) were treated as if they contain 16 carbon atoms for the purpose of calculating carbon-based yields and carbon balance, as these species were assumed to be formed by decarboxylation or carbonylation of C₁₆ products.

The selectivity of the products was calculated from the yield and the conversion using Equation 11:

$$S_i = \frac{Y_i}{X_{amide}} \quad (11)$$

where S_i is the selectivity of product i , Y_i the carbon based yield of product i and X_{amide} the conversion of the amide.

The carbon balance was calculated using Equation 12:

$$B_C = \frac{b_{amide,1}N_{C,amide} + \sum_i b_i N_{C,i}}{b_{amide,0}N_{C,amide}} \cdot 100\% \quad (12)$$

where $b_{amide,1}$ is the molality of the amide in the product mixture, b_i is the molality of product i in the product mixture, $b_{amide,0}$ is the molality of the amide in the zero sample, $N_{C,i}$ is the number of carbon atoms in product i and $N_{C,amide}$ is the number of carbon atoms in the amide.

Based on the results from the total N-content analyzer, the total nitrogen removal was calculated using Equation 13:

$$N_{removal} = \left(1 - \frac{N_1}{N_0}\right) \cdot 100\% \quad (13)$$

where N_1 is the nitrogen content (in mg/l) of the product mixture and N_0 is the

nitrogen content (in mg/l) of the feed solution.

The total oxygen removal was estimated from the GC-FID data using Equation 14:

$$O_{removal} = \frac{\sum_i b_{i,O} N_{O,i}}{b_{amide,0}} \cdot 100\% \quad (14)$$

where $b_{i,O}$ is the molality of oxygen-containing compound i in the products in mol/g, $N_{O,i}$ is the amount of oxygen atoms present in a molecule of i , and $b_{amide,0}$ is the molality of the amide model compound in the zero sample in mol/g.

E Additional catalyst characterization data

E.1 X-ray diffraction

The X-ray diffractograms for the NiMo/ γ -Al₂O₃ and NiMo/TiO₂ catalyst oxide precursors are shown in Figure S1. Only peaks related to the supports, γ -Al₂O₃ (ICDD 01-075-0921) and anatase TiO₂ (ICDD 01-083-5914), are present. The lack of crystalline Mo- and Ni-related species detected by XRD indicates that the Mo and Ni oxides present are amorphous, or that the crystallite size is below the XRD limit of detection. In either case, this implies that the Mo and Ni species are well-dispersed

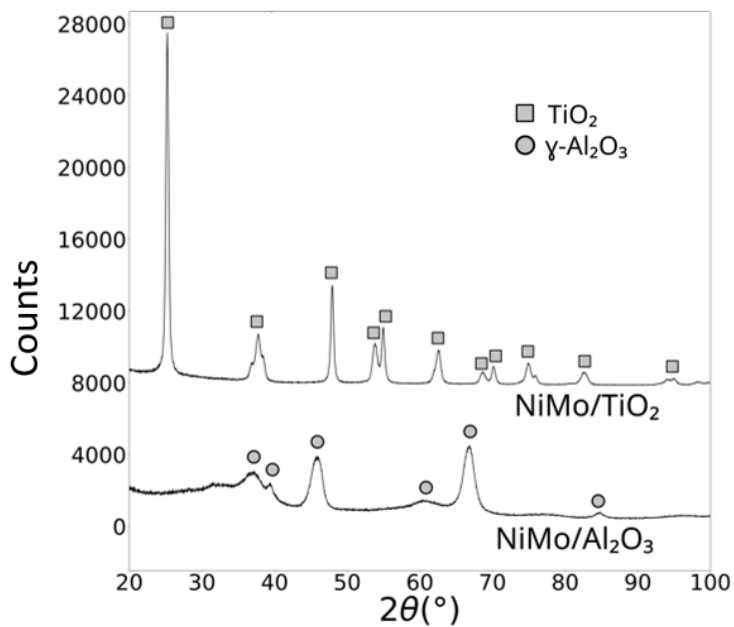


Figure S1

E.2 Transmission electron microscopy

Representative examples of TEM images of both catalysts are shown in Figure S2. In both images, the MoS₂ slabs can clearly be seen as dark lines on the lighter support material. Each line corresponds to one MoS₂ layer in the multi-layered slabs.

The TEM-derived MoS₂ slab length and stack height distributions are shown in Figure S3.

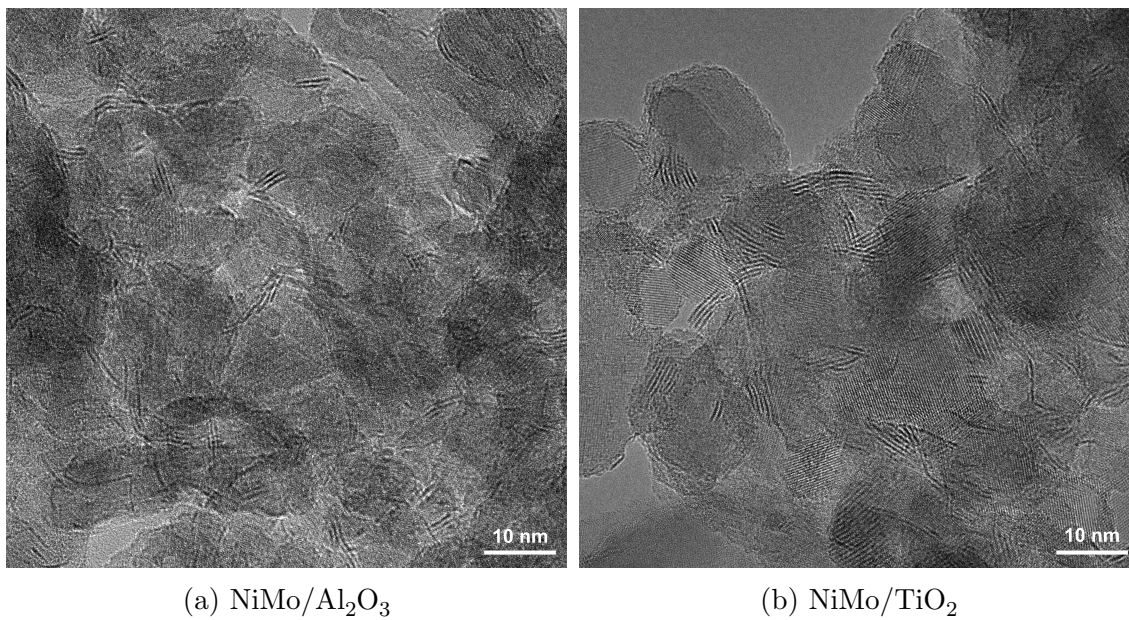


Figure S2: TEM images of a) NiMo/ γ -Al₂O₃ b) NiMo/TiO₂ catalysts

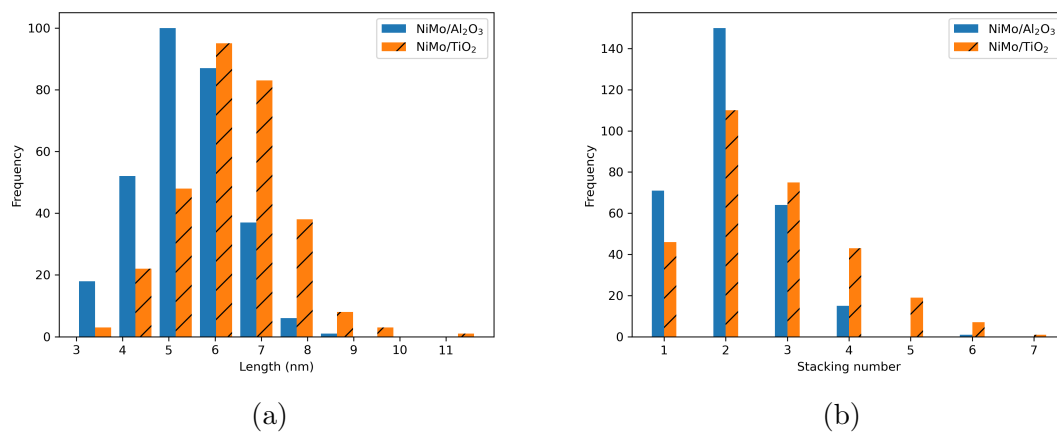


Figure S3: TEM-derived a) slab lengths and b) stack height distributions for the catalysts

E.3 X-ray photoelectron spectroscopy

Figures S4 and S5 show the XPS spectra for the Mo 3d and the Ni 2p_{3/2} regions.

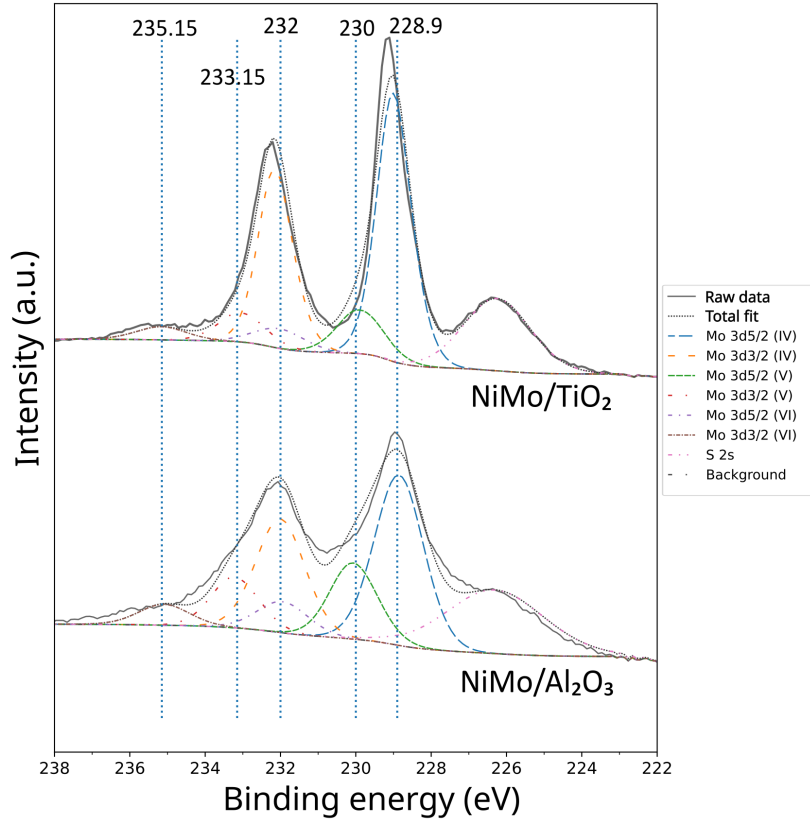


Figure S4: XPS spectra of the Mo 3d region for the NiMo/ γ -Al₂O₃ and NiMo/TiO₂ catalysts.

Table S2 shows the full atomic surface composition results from the XPS measurements. The results confirm that the surface concentration for Mo, Ni and S is substantially lower for NiMo/ γ -Al₂O₃ than for NiMo/TiO₂. As XPS is a surface-

sensitive method, this may imply that for NiMo/TiO₂, the active phase was enriched on the outer surface of the particles (egg-shell distribution) while for NiMo/ γ -Al₂O₃ the distribution was more homogeneous.

Table S2: Atomic surface composition from the XPS measurements for the supported NiMo sulfide catalysts.

Catalyst	Al %	C %	Mo %	Ni %	O %	S %	Ti %
NiMo/Al ₂ O ₃	36.7	6	1.7	0.2	52.1	3.3	0
NiMo/TiO ₂	0	10.4	5	0.9	53.1	10.6	20.1

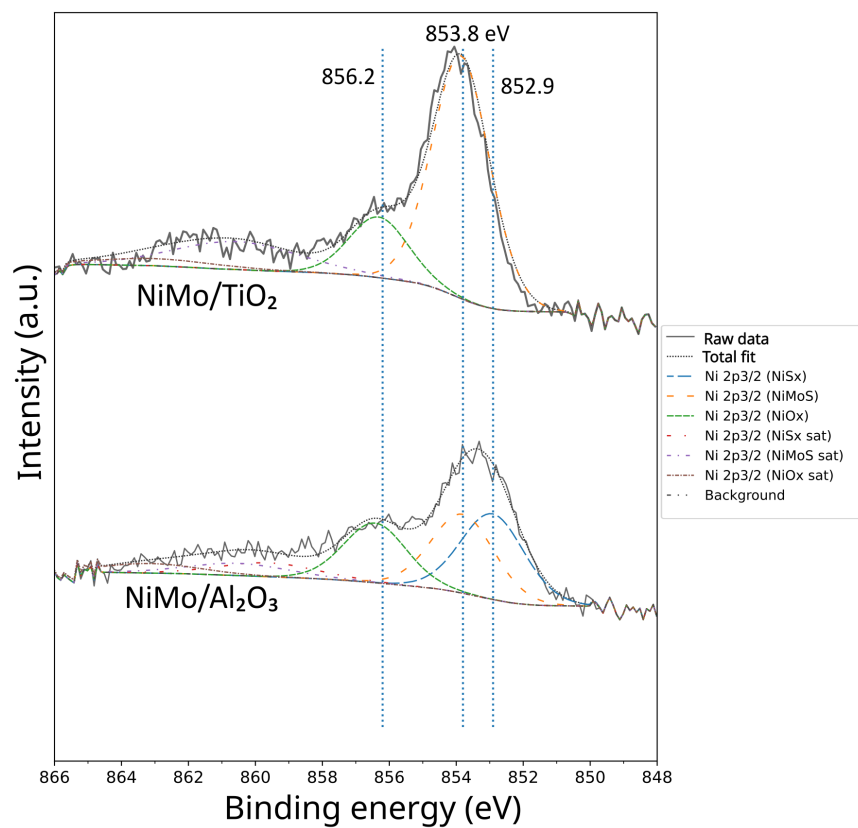


Figure S5: XPS spectra of the Ni 2p_{3/2} region for the NiMo/ γ -Al₂O₃ and NiMo/TiO₂ catalysts.

F Check for mass transfer limitations

Conversion, N-removal, O-removal, hydrocarbon yield and carbon balance with varying stirring speed in the batch reactor is shown in Figure S6. The data shows that Conversion, N-removal, O-removal and hydrocarbon yield all increase as the stirring speed is increased from 350 rpm to 700 rpm. Thus, external mass transfer limitations were likely present at 350 rpm. As stirring speed is increased further to 1050 rpm, no significant change is observed. As the stirring speed is increased even further to 1400 rpm, the carbon balance decreased substantially, likely due to the high stirring speed causing splashing and thus loss of model compound and products at the reactor walls and inlet pipes. Thus, the optimum stirring speed was found to be around 1000 rpm, since no external mass transfer was present and the carbon balance remained high, indicating little to no loss of model compound and products.

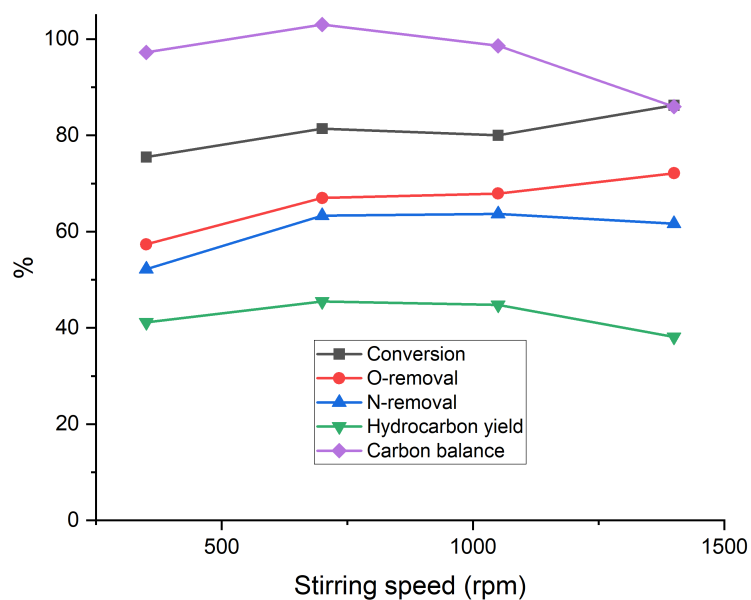


Figure S6: Conversion, N-removal, O-removal, hydrocarbon yield and carbon balance in the batch reactor as a function of stirring speed. Catalyst: NiMo/ γ -Al₂O₃, 300 °C, 70 bar, 1h reaction time.

G Thermal test results

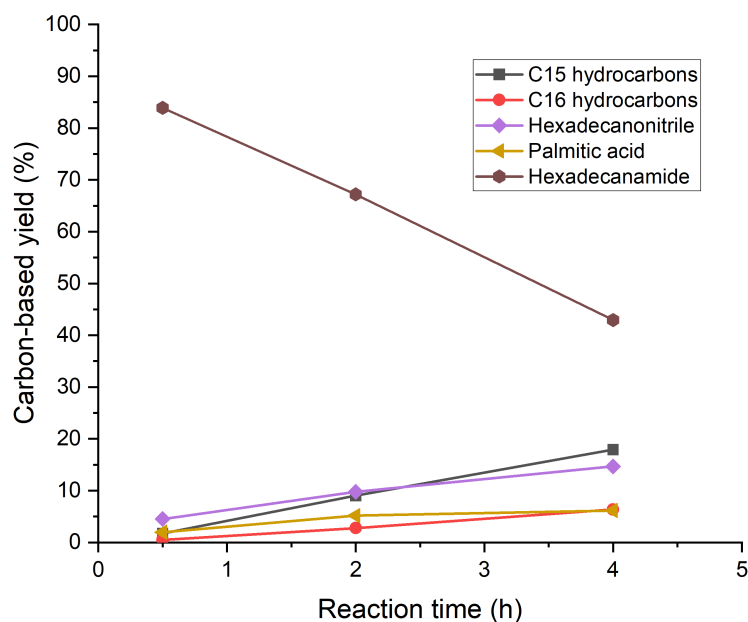


Figure S7: Carbon-based yield at different reaction times, with no catalyst in the batch reactor. Reaction conditions: 300 °C, 70 bar H_2 , 1000 rpm stirring. Solvent: decalin, reactant: hexadecanamide.

H Minor species detected

Figure S8 shows the yields of minor product species, with a maximum carbon-based yield of less than 5%, detected during the thermal tests. Small amounts of hexadecylamine and hexadecanethiol are present, and hexadecylhexadecanamide is formed at longer reaction times. The amine is likely formed through hydrogenation of the nitrile, while the thiol can be formed by a reaction of amine or nitrile with residual H_2S . Hexadecylhexadecanamide can likely be formed by condensation reactions between amine and carboxylic acid.

Figure S9 and Figure S10 show the yields of minor product species, with a maximum carbon-based yield of less than 10%, that were detected during the tests with

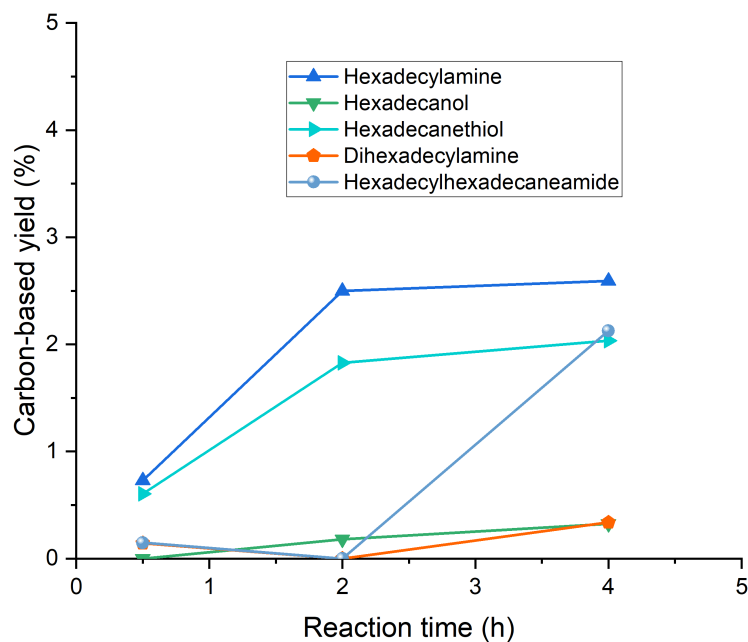


Figure S8: Carbon-based yield at different reaction times, with no catalyst. Reaction conditions: 300 °C, 70 bar H₂, 1000 rpm stirring. Solvent: decalin. Carbon balance was above 90% for all datapoints shown.

NiMo/ γ -Al₂O₃ and NiMo/TiO₂ catalysts. N-containing minor products include hexadecylamine and hexadecylhexadecanamide, while palmitic acid and hexadecanol are the O-containing products. As HDN and HDO proceeds, these species are converted into C15 and C16 hydrocarbon products. The presence of hexadecylhexadecanamide is noteworthy, as it confirms that condensation reactions can take place between the palmitic acid and hexadylamine. Thus, the two main reaction pathways (the HDO-HDN pathway and the HDN-HDO pathway) are not wholly separate, since the intermediates formed in each pathway can combine to form new products.

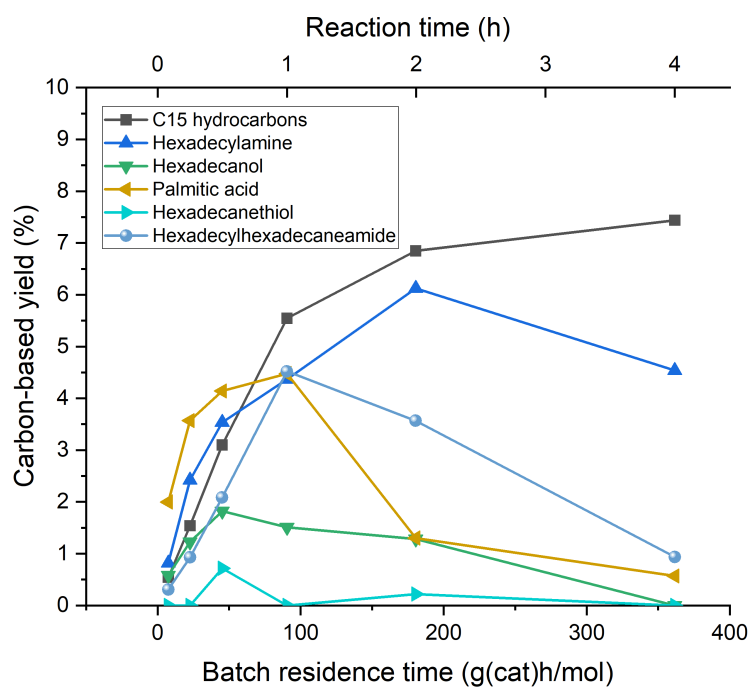


Figure S9: Carbon-based yield at different reaction times, with sulfided NiMo/ γ -Al₂O₃ catalyst. Reaction conditions: 300 °C, 70 bar H₂, 1000 rpm stirring. Solvent: decalin. Carbon balance was above 90% for all datapoints shown.

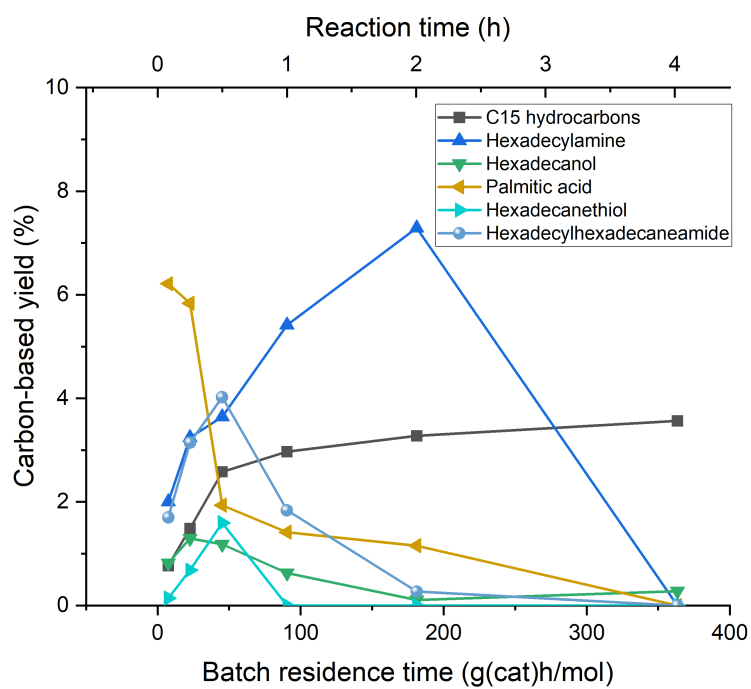


Figure S10: Carbon-based yield at different reaction times, with sulfided NiMo/TiO₂ catalyst. Reaction conditions: 300 °C, 70 bar H₂, 1000 rpm stirring. Solvent: decalin. Carbon balance was above 90% for all datapoints shown.

I Olefin and paraffin selectivities

During the reaction experiments (both in batch and flow conditions), several GC-FID peaks were detected close to the C16 paraffin (hexadecane) peak. GC-MS indicated that these peaks corresponded to C16 olefins, with fragmentation patterns giving a decent match for both 1-hexadecene and 2-hexadecene, although the presence of other isomers could not be ruled out. The experimental fragmentation pattern and the database pattern for 1-hexadecene are shown together in Figure S11.

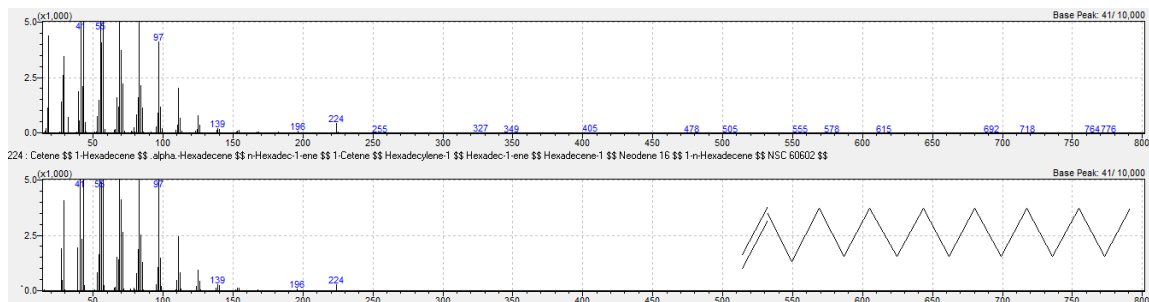


Figure S11: Experimental mass spectrum (electron ionization) of the major olefin-related GC peak.

In order to further confirm the identity of these peaks, a mixture of different C16 olefins were synthesized by dehydration of the C16 alcohol (hexadecanol). This was done by heating hexadecanol for 90 min at approximately 190 C with constant stirring in contact with a an Amberlyst 70 solid acid catalyst. The product mixture was dissolved in decalin, and analyzed by GC-FID. The relevant GC-FID peaks are shown in Figure S12. From Figure S12, it can be seen that the peaks present in the dehydrated hexadecanol mixture are a good match for the peaks present during the hydrotreating experiments. This match provides further evidence that the these peaks correspond to a mixture of different C16 olefins.

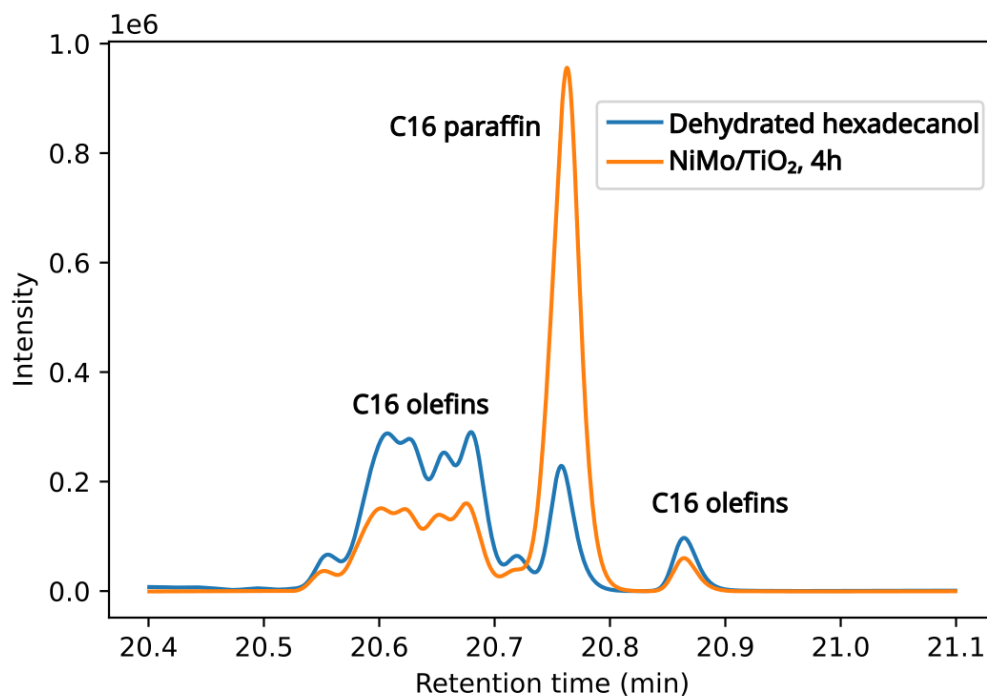


Figure S12: GC-FID chromatograms showing the C16 paraffin peak region for a batch reactor experiment (4h at 300 °C, NiMo/TiO₂ and the product mixture obtained after dehydration of hexadecanol.

Figure S13 shows the yields of the C16 paraffins and olefins for the NiMo/ γ -Al₂O₃ and NiMo/TiO₂ catalysts during the batch reactor experiments. The data shows that for both catalysts, a significant amount of olefin products are formed in addition to the paraffin. Both olefin and paraffin yields increase with increasing batch residence time, although at high batch residence times, the olefin selectivity decreases, likely due to olefin hydrogenation competing with olefin formation.

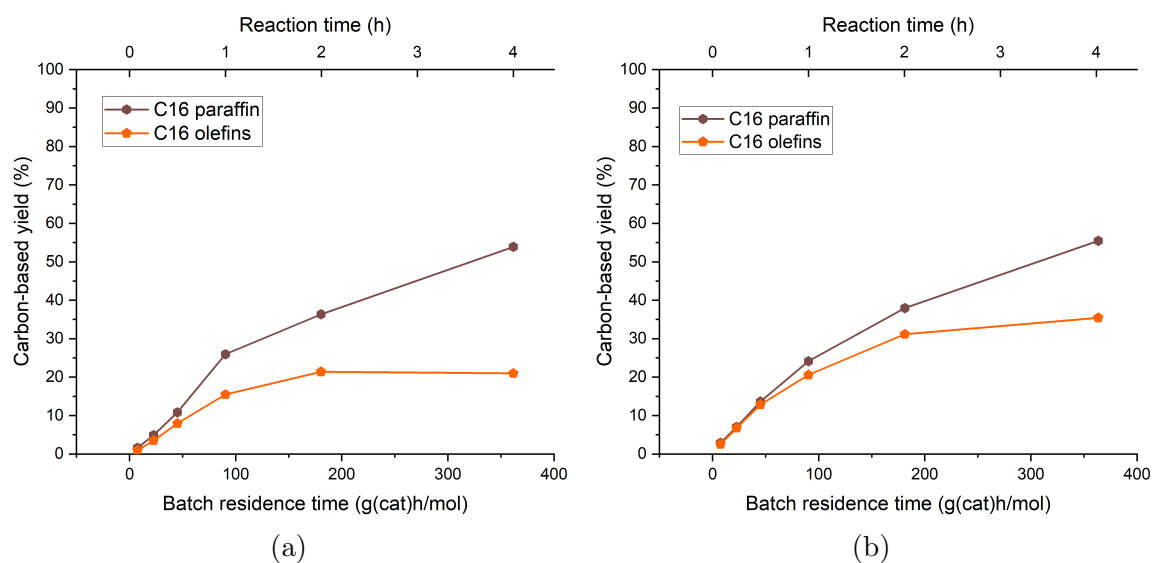


Figure S13: C16 paraffin (hexadecane) and C16 olefin yields as a function of batch residence time for a) NiMo/ γ -Al₂O₃ and b) NiMo/TiO₂.

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