

How does an acidic support affect the hydrotreatment of a gasoil with high nitrogen content?

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Supplementary information

GCxGC analysis

Method of GCxGC-NCD analysis of the gas oil feed

1. Injection: Samples were diluted in pure toluene until concentration 30-50 ppm before injection; Syringe size: 5 μ l; Injection volume: 0.5 μ l, on column injection
2. Inlets: Pressure: 350 kPa; Septum Purge Flow: 3ml/min
3. Oven: Programmed temperature: 60-260°C: 3°C/min and then 260°C for 30 min
4. Columns: 1st dimension: SPB5 27.5m x 0.25 mm x 1 μ m; 2nd dimension: SolgelWax 1.6m x 0.1mm x 0.1 μ m
5. Modulation : 12 seconds, trap at temperature of liquid nitrogen
6. Detector: NCD, detector temperature: 950°C; Acquisition rate: 100 Hz

Method of GCxGC-SCD analysis of the gas oil feed

1. Injection: 0.5 μ l, “on-column”, at 280°C
2. Columns:
 - Non-polar capillary column: stationary phase: HP-1 (100% dimethylpolysiloxane), length : 30 meters ; internal diameter : 0.32 mm ; film thickness: 0.1 μ m
 - Polar capillary column: stationary phase: Solgel Wax (polyethylene glycol); length: 1 meter; internal diameter: 0.1 mm; film thickness: 0.1 μ m
 - Program of temperature: 40°C for 5 min, then 4°C/min to 300°C, 300°C for 5 min
3. Carrier gas: Helium, inlet pressure: 13 psi, outlet flow rate: 1 ml/min

4. Detector: Sulfur Chemiluminescence Detector, at 800°C, acquisition rate: 100Hz
5. Modulation: 14 seconds, trap at temperature of liquid nitrogen

Estimation of the characteristic times of external and internal mass transfer in the fixed bed reactor

The characteristic time of external mass transfer was estimated using the empirical correlation for the Sherwood number (Sh):

$$t_{ext} = \frac{1}{k_L \cdot a} = \frac{d_p^2}{6 \cdot Sh \cdot D_m}$$

$$Sh = \frac{k_L \cdot d_p}{D_m} = 2 + 0.6 Re^{1/2} Sc^{1/3}$$

k_L is the rate of external diffusion, a is the volumetric surface area of the mass transfer, d_p is the diameter of catalyst particle, D_m is the molecular diffusion coefficient of the reacting molecule (quinoline was taken as example).

The Reynolds (Re) and Schmidt (Sc) numbers were calculated by the well-known formulas:

$$Re = \frac{u_v \cdot d_p}{\nu} \text{ and } Sc = \frac{\nu}{D_m}$$

u_v is the rate of liquid feed through the reactor and ν is the kinematic viscosity of the stream.

The molecular diffusion coefficient of quinoline (D_m) was calculated by the empirical Wilke-Chang correlation:

$$D_m = 7.4 \times 10^{-8} \cdot \frac{(\Theta \cdot M_B)^{1/2} \cdot T}{\mu_B \cdot V_A^{0.6}}$$

Θ is the dimensionless solvent association coefficient, equal to unity for hydrocarbons; M_B is the molecular mass of the hydrocarbon solvent (g/mol); V_A is the molar volume of quinoline at its boiling point (m³/mol); T is the temperature at reaction condition (K) and μ_B is the dynamic viscosity of hydrocarbon solvent (cP).

Table S1: Data for estimation of external mass transfer coefficient

Dimensionless solvent association coefficient	θ		1
Molecular weight of the gas oil feed	M_B	g/mol	219.86
Temperature	T	K	633.15
Kinematic viscosity at 633K	ν	cSt	0.409
density of the gas oil feed at 633K	d	g/ml	0.614
Dynamic viscosity of the gas oil feed at 633K	μ_B	cP	0.251
Molar volume of quinoline at its boiling point	V_A	m ³ /kmol	0.1179
Molecular diffusion coefficient of quinoline	D_m	cm ² /s	1.58E-4
Schmidt number	Sc		2583
Diameter of reactor		cm	1.8
Feed flow rate		m ³ /s	8.3E-10
Feed superficial velocity	u_v	m/s	3.3E-6
Catalyst grain diameter	d_p	μm	80
Reynold number	Re		6.41E-6
Sherwood number	Sh		2.021
External diffusion velocity	k_L	m/s	4.0E-4
Superficial surface of catalyst grain	a	m ² /m ³	75000
Coefficient of external transfer	$k_L a$	s ⁻¹	29.97
characteristic time of external mass transfer	$1/k_L a$	s	0.033

The characteristic time of internal mass transfer was estimated from

$$t_{\text{int}} = \frac{d_p^2 \cdot \tau}{6 \cdot \varepsilon \cdot D_m}$$

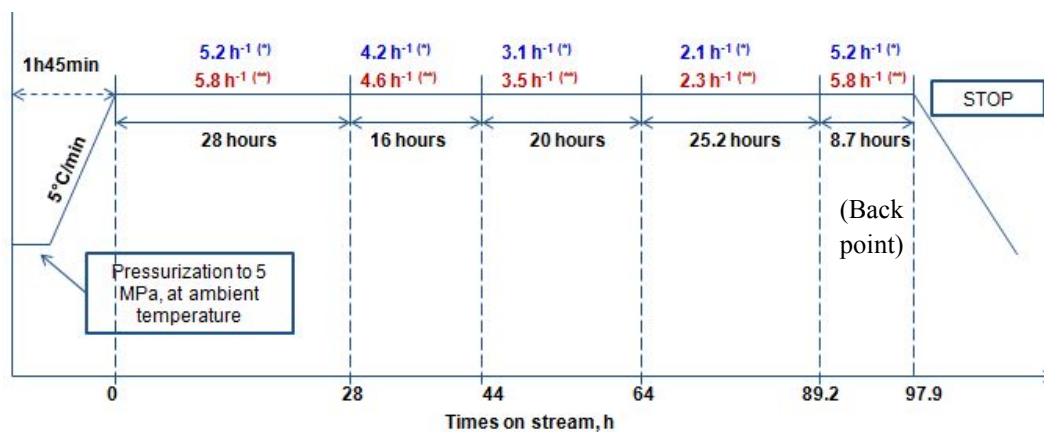
ε and τ are the porosity and the tortuosity of the catalyst particle. Since the tortuosity of the catalyst is difficult to measure, the porosity and tortuosity of the support were used as a surrogate.

Table S2: Data for estimation of internal mass transfer coefficient

Porosity	ε		0.72
Tortuosity	τ		2.9
Molecular diffusion coefficient of quinoline	D_m	cm ² /s	1.58E-04
Catalyst grain diameter	d_p	μm	80
characteristic time of internal mass transfer	t_{int}	s	0.045

Protocol of catalytic tests

A protocol of a catalytic test is illustrated by the following figure. A value of temperature was fixed during each run, *i.e.* 350, 360 or 370°C. During each run, four operating conditions differ from LHSV values, *i.e.* in the range of 2-6 h⁻¹, was performed. At the end of each run, deactivation of the catalysts was evaluated by returning to the initial LHSV.



(*): LHSV for tests over NiMo(P)/Al₂O₃

(**): LHSV for tests over NiMo(P)/ASA

Calculation of rate constants – deactivation

In order to quantify deactivation, a rate law with a reaction order of n with respect to S or N compounds was used:

$$dC / dt = -k_{app} [C]^n \quad (\text{Equation 3})$$

Integration of this equation over residence time yields:

$$f(n) = \frac{1}{n-1} \left(\frac{1}{[C]_{out}^{n-1}} - \frac{1}{[C]_{in}^{n-1}} \right) = \frac{k_{app}}{LHSV} \quad (\text{Equation 4})$$

where k_{app} is the apparent rate constant at given temperature ($wppm^{1-n} \cdot h^{-1}$), $[C]_{in}$ and $[C]_{out}$ are the concentrations of either sulfur or nitrogen in the feed and in the product (wppm), respectively.

For the HDS conversion, the data were best described by a reaction order of 1.77, for HDN the apparent reaction order was 1.39. Using these apparent reaction orders, we could calculate the apparent rate constants at the beginning and at the end of the catalytic test and deduce the degree of deactivation.

Table S3: Determination of the loss of HDS and HDN activity for 2 catalysts

	NiMo(P)/Al ₂ O ₃	NiMo(P)/ASA
$k_{i,HDS}$, (wppm ^{-0.79} ·h ⁻¹)	0.0426	0.0239
$k_{f,HDS}$, (wppm ^{-0.79} ·h ⁻¹)	0.0364	0.0209
Loss of activity	15%	13%
$k_{i,HDN}$, (wppm ^{-0.39} ·h ⁻¹)	0.7752	0.7076
$k_{f,HDN}$, (wppm ^{-0.39} ·h ⁻¹)	0.7341	0.6403
Loss of activity	5%	10%

Hydrotreating of an SRGO + LCO mixture

The NiMo/Al₂O₃ and NiMo/ASA catalysts were compared in supplementary test with a gasoil feed prepared from a mixture of straight run gas oil (SRGO) and Light Cycle Oil (LCO).

Properties of the feed

Table S3 shows the global nitrogen and sulfur content of the feed. Compared to the SRGO + CGO feed, the nitrogen and sulfur concentration was much lower. The fraction of basic nitrogen was only 13%, which is typically low for LCO feeds.

Table S4: Properties of gasoil feed prepared from a mixture of SRGO and LCO

	SRGO + LCO
Total nitrogen (wppm)	334 ± 25
Basic nitrogen (wppm)	44 ± 3
Total sulfur (wt %)	0.38
Density at 15°C (g/ml)	0.899

Table S5 : Analysis of the sulfur compounds in the gasoil mixture

Total sulfur (ppm)		3778	
Sulfur Family distribution	% of total sulfur	(ppm of sulfur)	(ppm of compound)
Alkyl-thiophenes + sulfides	0.0%	0	-
BT	0.4%	13	56
C1-BT	5.2%	198	918
C2-BT	11.6%	437	2218
C3-BT	10.4%	394	2173
C4-BT	11.6%	439	2613
DBT + NAPHTO	4.5%	171	986
C1-DBT	15.5%	586	3633
C2-DBT	16.3%	618	4098
C3-DBT+	24.4%	920	6508
Alkyl-thiophenes + sulfides	0.0%	0	-
Totals BT family	39.2%	1483	7977
Totals DBT family	60.8%	2295	15225

Table S4 shows the detailed analysis of the sulfur compounds in the feed. Compared to the other feed, the fraction of DBTs was very high and there were hardly any “easy to convert” sulfur compounds (thiophenes and sulfides).

The distribution of nitrogen compounds was determined by GCxGC NCD. Carbazoles and to a lesser extent indoles were the dominating nitrogen species. Note that the fraction of basic nitrogen according to GCxGC-NCD was only 6%, i.e. significantly lower than the value obtained by potentiometric titration. The mismatch can be ascribed to an overlap of the elution zones of indoles and pyridines.

Table S6 : Analysis of the nitrogen compounds in the gas oil mixture

Family	% m/m N
CARBAZOLES	77.45
TETRAHYDROCARBAZOLES + ACRIDINES	0.58
INDOLES	15.87
QUINOLEINES	3.72
ANILINES	2.38
PYRIDINES	0.00
TETRAHYDROQUINOLEINES	0.00

Catalytic tests

The tests with the SRGO + LCO feed were carried out in Flowrence fixed bed reactor, at an LHSV of 1 or 2 h⁻¹, a H₂/hydrocarbon ratio of 640 and a pressure of 80 bar. The temperature was varied between 275 and 285°C. These temperatures are unusually low for hydrotreating, but at higher temperature HDN is complete at 80 bars and a comparison of HDN activity is not possible (and the unit does not allow working at much higher LHSVs).

The effluents were analyzed by UV Fluorescence to determine total sulfur content and by chemiluminescence (ANTEK 9000NS) to determine the total nitrogen content. The basic nitrogen content was determined by potentiometric titration (ASTM D2896).

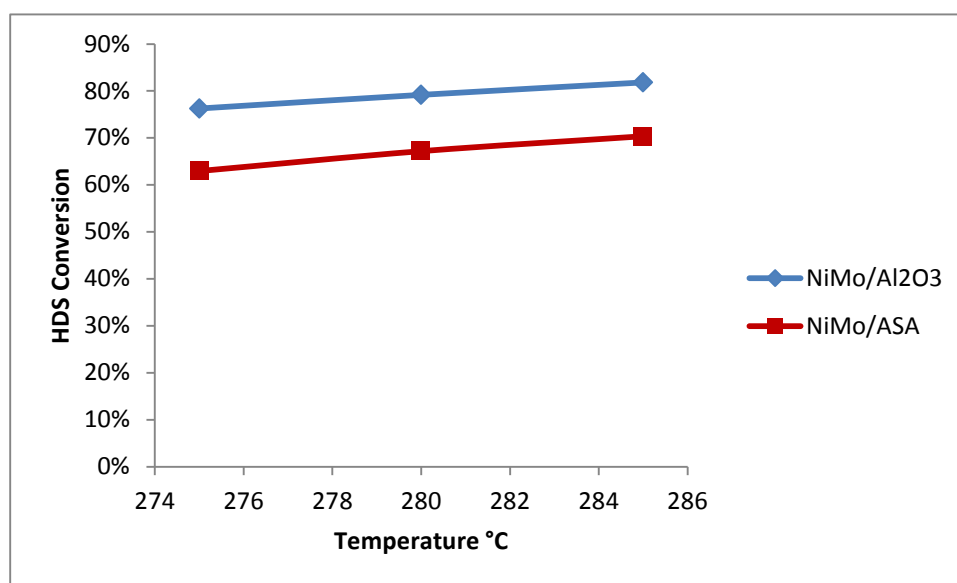


Figure S1 HDS conversion of the SRGO + LCO feed over NiMo/Al₂O₃ and NiMo/ASA.

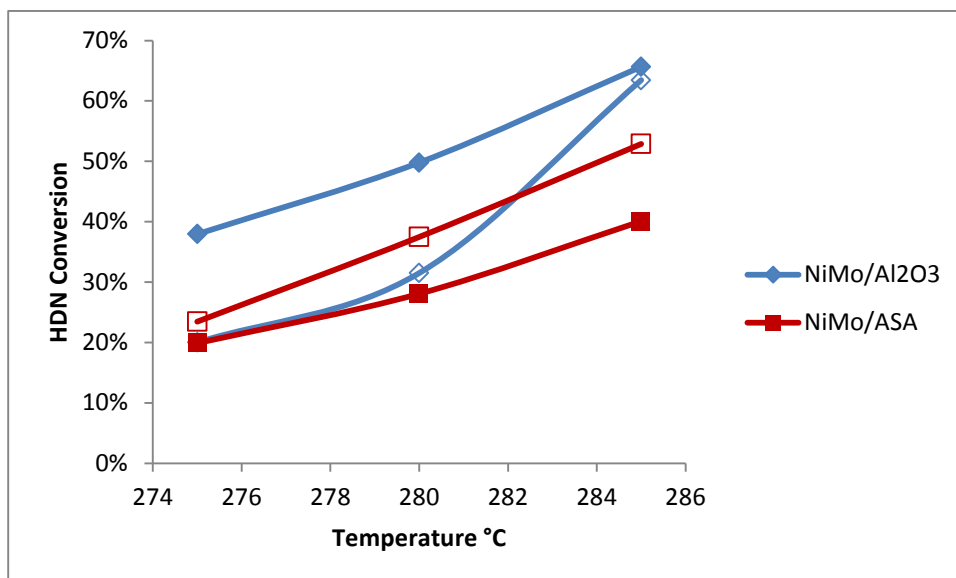


Figure 2 HDN conversion SRGO + LCO feed over NiMo/Al₂O₃ and NiMo/ASA. Full symbols: total nitrogen; empty symbols: basic nitrogen.

Figure S1 shows that the ASA-supported catalyst was less active in HDS than the alumina-supported catalyst, as for the CGO-containing feed. The ASA-supported catalyst was also considerably less active in HDN (Figure S2). The ASA-supported catalyst preferentially converted the basic nitrogen species, while the Al₂O₃-supported catalyst preferentially converted neutral nitrogen species.