

Electronic supplementary information (ESI)

Synthesis of highly-uniform titania overcoats on a mesoporous alumina catalyst support by atomic layer deposition and their application in hydroprocessing

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Catalyst preparation and performance testing

The TiO₂-Al₂O₃ supports that were prepared after 1, 2 and 3 ALD cycles with TTIP were used for the preparation of CoMo hydroprocessing catalysts. As a comparison, the Al₂O₃ support of the deposition experiments was used without any modification in order to prepare a reference CoMo/Al₂O₃ catalyst. The different supports were loaded with active metals by pore volume impregnation with a solution prepared from MoO₃ (Climax, pure oxide), CoCO₃ (Chemlock, high purity, 46.7 wt% Co) and H₃PO₄ (Sigma Aldrich, 85 wt% solution in water). The CoCO₃ was suspended in distilled water at room temperature and H₃PO₄ was added incrementally to prevent extensive gas formation. Then, half of the required amount of MoO₃ was added and the suspension was heated to 92 °C, while preventing evaporation of water. Finally, the rest of the MoO₃ was added and the mixture was allowed to react until a clear solution was obtained. Impregnation was carried out at room temperature.^{1, 2} The effective pore volume of the TiO₂/Al₂O₃ support was determined by the amount of water that could be absorbed. The volume of the solution used for impregnation was set to be 105% of the pore volume, as determined in this way. The impregnated particles were dried in a hot air flow while being kept in constant motion, until the particles appeared dry. Finally, the particles were dried at 120 °C in a static oven for 14 hours. The reference catalyst had a MoO₃ loading of 24 wt%. All catalysts have the same molar ratio of Co:Mo (0.40) and P:Mo (0.34). The metal loading of the other catalysts was adjusted with the aim of achieving an equal volumetric metal loading in the testing reactors. Actual MoO₃ loadings, as determined by XRF can be found in Table S2.

The catalysts were tested in a fixed bed multi-tubular reactor set-up for hydroprocessing performance testing. Catalysts were tested as particles from crushed extrudates, size-selected in 125-300 μm range. For all catalysts, 0.9 ml of the catalytic material was measured and loaded in the reactor (the reactor diameter was 7 mm). The corresponding catalyst weights and the amount of MoO₃ that was eventually present in each reactor test run can be found in Table S2. Although

the aim was to evaluate the catalyst at equal volumetric metal loading, this is challenging as packing artefacts can result in differences in metal loading between reactors at this small scale. In the end, this approach was successful, with only the sample based on the support overcoated by one TiO₂ deposition cycle showing a significant deviation.

The relevant properties of the light gas oil (LGO) used in the testing can be found in Table S1. The catalysts were sulfided in-situ with an LGO spiked with dimethyl disulfide (DMDS) resulting in a pre-sulfiding feed with 2.5 wt% S at 320 °C, 45 bar, a liquid hourly space velocity (*LHSV*) of 3.0 h⁻¹ and a H₂/LGO ratio of 300 NI/l. The catalysts were exposed to LGO at 45 bar and a H₂/LGO ratio 300 NI/l at different feed rates and temperatures, before activity evaluation at 350 °C and a *LHSV* of 2.0 h⁻¹ took place by gas chromatography.

As any conventionally used oil fraction, the LGO used in this study includes a range of different S-containing molecules, ranging from simple thiophene-like molecules with a high reaction rate for HDS to refractory substituted dibenzothiophenes which have a much slower rate of reaction. In HDS performance testing, the apparent HDS reaction order of different catalysts is determined based on the total S concentration in the feed and the test product (regardless of the type of S-containing molecules present). As a result, although the reaction order for HDS of the individual S-compounds is 1, the observed reaction order based on the total S-concentration of feed and product ($s_{feed} \cdot s_{product}$) can be significantly higher than 1, depending on the test conditions (conversion, pressure, temperature and feed) used.³⁻⁵

For the test conditions applied in this study, we have determined —based on extensive testing, analysis of the feed and products and modelling of the results— that at our conditions the representative reaction order for HDS (*n*) is 1.3. Using this equation order, and Equation S1, the volumetric HDS reaction order constants (k_{HDS}) were determined for the different catalysts. Subsequently, for each catalyst, the relative volumetric activity ($^{RVA}_{HDS}$) was calculated, where the catalyst without TiO₂ overcoat was used as reference. For this type of catalysts, this is often the most relevant property, as it determines the activity that can be obtained in a certain fixed reactor volume. Finally, the volumetric activities were normalized on metal basis, yielding the relative metal-based activity ($^{RMA}_{HDS}$) by taking into account the amount of MoO₃ that was present in each reactor during the test runs. This value shows how effectively the metals are being utilized in the different catalysts. The amount of metals used has a direct influence on the catalyst production cost. The results of the tests are summarized in Table S1 and Table. S2.

$$k_{HDS} = \frac{LHSV}{n-1} \cdot \left(\frac{1}{s_{product}^{(n-1)}} - \frac{1}{s_{feed}^{(n-1)}} \right) \quad \text{(Equation S1)}$$

Table S1: Properties of the light gas oil (LGO) feed used for HDS catalytic performance evaluation, including S/N/H concentrations, density, initial boiling point (IBP), final boiling point (FBP) and boiling point distribution

Composition			Boiling point distribution			
Sulphur, S	11875	[ppm]	Recovery	Boiling point	Recovery	Boiling point
Nitrogen, N	231	[ppm]	[wt%]	[°C]	[wt%]	[°C]
Hydrogen, H	13.09	[wt%]	IBP	158.7	60	411.0
Density			10	253.9	70	342.6
(at 15.6 °C)	0.861	[g/ml]	20	280.5	80	355.5
			30	297.4	90	368.4
			40	311.7	95	381.2
			50	326.2	FBP	390.7

Table S2: Properties of the catalysts used in HDS performance evaluation and the observed conversion (relative volume activity, RVA) and activity (activity per Mo atom, RMA)

ALD cycles	TiO ₂ content	catalyst in reactor	MoO ₃ content	MoO ₃ in reactor	S content	k_{HDS}	RVA_{HDS}	RMA_{HDS}
	[wt%]	[g]	[wt%]	[g]	[ppm]		[%]	[%]
0 (ref.)	0	0.744	24.0	0.179	69	2.21	100	100
1	7	0.871	25.0	0.218	21	3.41	155	127
2	14	0.881	20.7	0.182	28	3.08	140	137
3	20	0.924	19.5	0.180	44	2.61	118	118

Catalyst characterization

Samples for SEM-EDX analysis were prepared by embedding the particles in a resin. The block with the embedded particles was then ground down and polished to effectively obtain a sample exposing the cross sections of the particles and yielding a flat surface. Measurements were done with a Zeiss EVO MA15-Noran system 7 microscope.

The sample preparation method used yields a flat surface and certainly, towards the center of the particles, the samples can be regarded as homogeneous in the direction perpendicular to the surface. The total signal obtained for the different elements present (Al, Si, Ti from the support) was normalized to 100%, taking into account the molecular weight of the corresponding oxides. By calibration to samples of known elemental composition, a semi-quantitative method is obtained, that allows determination of the local TiO₂ content of the particles with a precision of ± 1 wt%.

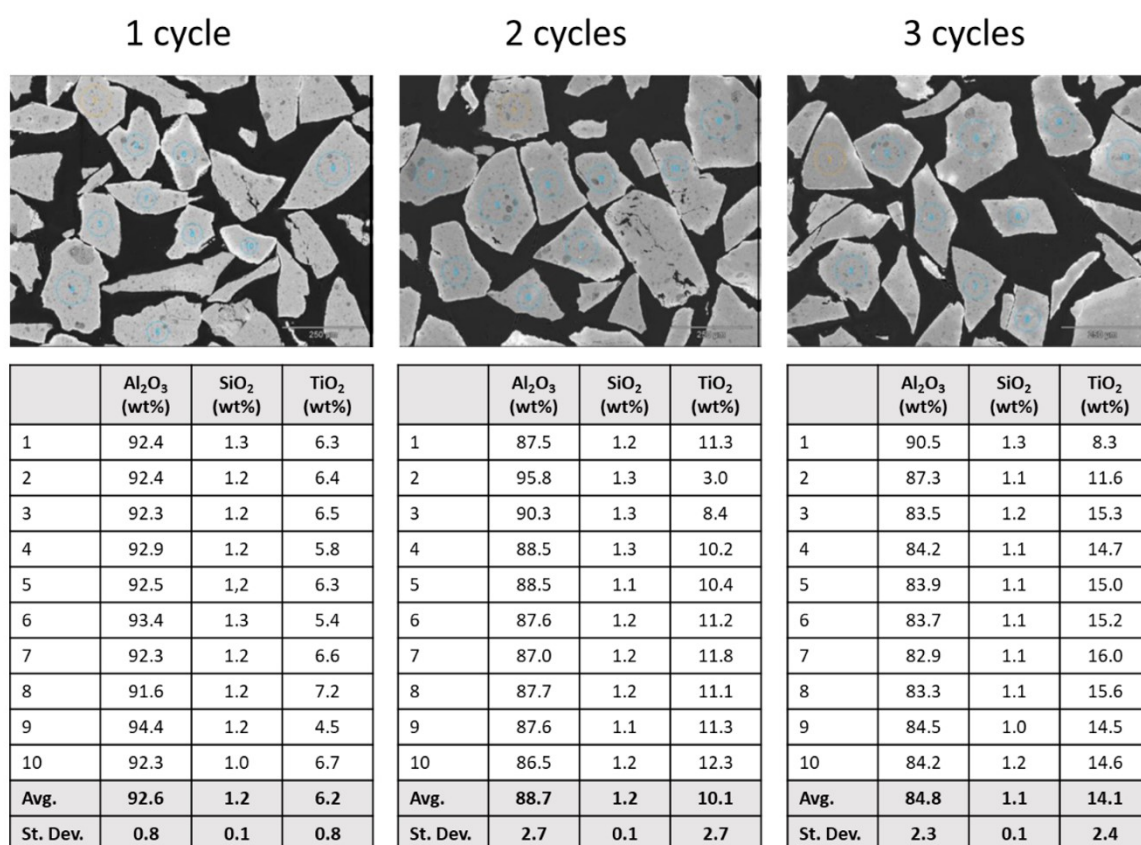


Fig. S1: SEM-EDX spot measurements near the center of the TiO₂-Al₂O₃ particles after overcoating corresponding to 1, 2 and 3 TTIP ALD cycles.

Using this method, the average concentration of TiO₂ near the center of the particles was determined by taking spot measurements of 10 different particles (Fig. S1). The values are used for the correlation with the bulk concentration as determined by ICP-OES.

The composition of the CoMo-TiO₂/Al₂O₃ catalysts was determined using XRF. The sample material was calcined for 30 minutes at 450 °C. Subsequently, it was fused with lithium borate (ICPH Fluorex 65 borate flux) to obtain a homogeneous melt. These melts were poured into a casting dish to form flat glass-beads. These beads were analysed by wavelength dispersive X-ray spectrometry (Malvern Panalytical Axios). The corrected intensities are related to the concentrations of aluminium oxide, titanium oxide, molybdenum oxide, cobalt oxide in the disk and, knowing the mass ratio of sample material and flux, to the concentrations in the sample applying an external calibration. For this calibration, standard fused disks were prepared from high purity materials.

To determine the change in surface area upon TiO₂ deposition, a hexane adsorption method developed in-house by Ketjen,⁶ that allows one to use extremely small sample quantities, was used. A portion of 20 mg of a sample was weighed into Mettler Toledo thermogravimetric

analysis (TGA) balance. The sample was heated to 600 °C and allowed to cool down to 300 °C in N₂ flow (80 ml/min). Subsequently, the sample was exposed to a flow of hexane in N₂ (80 ml/min, partial pressure of 80 Torr of hexane) and the weight increase of the sample by hexane adsorption was recorded as a function of temperature, while the sample was cooled down at a rate of 2.5 °C/min. From this data, a plot was constructed with the excess surface work (ESW) as a function of the amount of hexane adsorbed. The hexane adsorption (in μmol/g) for the formation of a monolayer of hexane was determined by determining the minimum of the ESW in this plot as explained in the patent application.⁶

For TEM sample preparation, the ALD-modified support and final catalyst samples were rinsed with toluene, ground in a mortar and dried at 150 °C in vacuum to remove residual toluene. After drying, the samples were embedded in an Ultra-Low Viscosity Kit (ULVK) epoxy resin and cured at 60 °C under pressure (2.5 bar) for at least 48 hours. After curing, specimens with a thickness of about 60 nm were obtained by microtome cutting at room temperature. The slices were collected on a water surface and transferred to carbon coated grids (400 mesh grids). Measurements were carried out using Osiris microscope equipped with an FEG gun at an acceleration voltage of 200 kV with an energy dispersive x-ray spectroscopy (EDX) detection system. Data analyses of TEM-EDX, such as elemental mapping, were carried out in Esprit 1.9 software.

References

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