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

Jacob A. Moulijn, ^{a,b} J. Ruud van Ommen, ^b Aristeidis Goulas, ^b David Valdesueiro, ^b Jana Juan-Alcañiz, ^c Kar-Ming Au-Yeung, ^c Leo Woning ^c and Jaap A. Bergwerff ^c

The feasibility of gas phase deposition using a Ti alkoxide precursor for precise surface modification of catalysts was demonstrated by modifying a mesoporous alumina support with a Ti oxide overcoat. Titanium tetra-isopropoxide yields a Ti oxide layer that covers homogeneously the alumina surface. Uniformity of the deposited TiO_2 was verified by SEM-EDX, on both intra-particle and inter-particle levels. Only a few atomic layer deposition (ALD) cycles were required in order to obtain Ti contents with a relevance for industrial application. The pore size distribution of the overcoated catalyst support was barely affected by the coating process. Synthesized CoMo catalysts based on the Ti-alumina carrier showed up to 40% higher activity compared to a catalyst supported on pristine alumina, in hydroprocessing under industrial testing conditions. The TiO_2 coating appeared to be stable, showing no agglomeration characteristics after reaction as corroborated by TEM-EDX. ALD provides a scalable route with low waste generation for the production of precisely structured $\text{TiO}_2\text{-Al}_2\text{O}_3$ hydroprocessing catalyst supports.

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Introduction

Hydroprocessing catalysts play a central role in oil refineries as they enable the reduction of the sulphur and nitrogen content of the refining products. Also, in the production of fuels from biogenic sources and the refining of waste recycle streams, hydroprocessing catalysts hold an important contribution. Typical catalyst materials are combinations of molybdenum or tungsten oxide, promoted by cobalt or nickel oxide and supported on a porous carrier, often alumina (Al_2O_3).^{1–3} Following increasingly stringent environmental regulations, there are continuous initiatives for research of more active catalysts. Titanium oxide (TiO_2) has emerged as a promising support, outperforming alumina.^{4–9} It has been shown that the interaction of the active phase and the support is lower for TiO_2 than for Al_2O_3 .¹⁰ As such, this reduced interaction can explain the higher activity of TiO_2

based catalysts. Another explanation put forward by Coulier *et al.*¹¹ has shown that TiO_2 sites act as promotor sites, similar to Ni and Co.

Unfortunately, compared to aluminas, titanium oxides generally have small surface areas and a poor thermal stability,¹² which negatively affects catalyst performance. The negative effect of the low surface area becomes especially pronounced at the high active metal loadings, which are required for the production of ultra-low-sulphur diesel (ULSD). Thus, it is difficult to assess the true potential of TiO_2 as a support for industrial hydroprocessing catalysts. An elegant alternative design proposal involves the modification of a commercially available alumina with favourable porosity characteristics (pore volume, pore size distribution, specific surface area) with a thin overcoat of titanium oxide. In this way, the effect of TiO_2 addition to hydroprocessing performance can be assessed without the interfering effect of the pore structure. One of our goals was to provide a fair comparison of titania and alumina for application as support for hydroprocessing catalysts.

Solvent-based methods are conventionally applied in the synthesis of hydroprocessing catalysts. We opted for the use of atomic layer deposition (ALD), a highly precise gas phase deposition technique, in synthesizing a $\text{TiO}_2\text{-Al}_2\text{O}_3$ support of a high-quality CoMo hydroprocessing catalyst.^{13–17} The

^a Delft IMP B.V, Molengraaffsingel 8, 2629 JD Delft, The Netherlands

^b Delft University of Technology, van der Maasweg 9, 2629 HZ Delft, The Netherlands

^c Ketjen, Nieuwendammerkade 1-3, 1022 AB Amsterdam, The Netherlands

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applicability of ALD for the preparation of heterogeneous catalysis and their respective catalytic supports has been discussed extensively in literature.^{13,18} For hydroprocessing, ALD was successfully implemented for the synthesis of a Pd-based catalyst¹⁹ and the modification of a Pd catalyst with a TiO₂ overcoat.²⁰ Furthermore, MoO₃ active phase growth on mesoporous alumina by ALD and its application in oxidative desulphurization has been reported.²¹ ALD synthesis was anticipated to lead to a homogeneously distributed Ti layer, fully covering the accessible surface of the support. Moreover, contrary to conventional used synthesis methods it provides the possibility to avoid the use of solvents, thus drastically minimizing the generation of synthesis process-related waste.²²

In early ALD studies, Lakomaa *et al.*²³ first reported the growth of a TiO₂ oxide coating onto a mesoporous silica catalyst support by TiCl₄ and H₂O. Haukka *et al.*^{24,25} implemented a single TiCl₄ exposure on mesoporous SiO₂ catalyst support. After thermal decomposition of the deposited species, scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) of silica particle cross-sections revealed an even distribution of the TiO₂ particles, with no enrichment of the outermost surface of the support.²⁵ In the follow-up work of Lakomaa *et al.*,²⁶ the homogeneity of the Cr and Ti species spatial distribution was again verified. A high ratio of Cl/Ti was observed in all cases, and residual Cl was only reported to be removable by thermal treatment with H₂O vapor at 450 °C.

In addition, Haukka *et al.*²⁷ described the modification of mesoporous γ -alumina by titanium tetra-isopropoxide (TTIP). Lindblad *et al.*²⁸ deposited TiO₂ into porous Al₂O₃ using TTIP and air at 450 °C. Keränen *et al.*²⁹ used TTIP to modify mesoporous SiO₂ with TiO₂, in order to prepare a catalyst support for subsequent vanadia deposition. Treatment at elevated temperature for the ligand removal was required, similar to the work based on the TiCl₄ precursor. Lu *et al.*³⁰ and Yang *et al.*³¹ described the growth of TiO₂ into silica gel powder, using TTIP and H₂O at lower temperature (150 °C and 200 °C respectively). SEM-EDX revealed that the Ti species were deposited more effectively on the outer surface of the SiO₂ support.³¹

Catalyst performance can be heavily influenced by the existence of impurities that can strongly absorb into the support surface. Such is the case for the Cl ligands of the Ti halide precursor. Although a ligand removal step at high temperature can eliminate the Cl impurities, ALD schemes operated at -relatively- low temperatures are deemed more feasible for large-scale catalyst synthesis. For that reason, we selected the alkoxide precursor, titanium tetra-isopropoxide for our ALD scheme. A comprehensive list of TTIP-based ALD processes for TiO₂ growth is reported in the review article of Niemelä *et al.*³²

In summary, the objective of this study was (i) to demonstrate the feasibility of TTIP as ALD precursor for the synthesis of highly-uniform overcoats on mesoporous catalyst supports at deposition temperatures that enable feasible

large-scale catalyst synthesis, and (ii) to establish the superior properties of titania compared to alumina as support for hydroprocessing catalysts.

Experimental

Overcoat synthesis by ALD

The coating experiments were carried out in a fluidized bed reactor³³ operated at atmospheric pressure. This reactor is composed of a glass column of 26 mm internal diameter and 500 mm height, supported on a pneumatically vibrated piston to assist the fluidization of the powder. Four infrared lamps placed around the column were used to heat up the reactor to the reaction temperature, while a type-K thermocouple inserted inside the column enabled control of the reaction temperature. The fluidization gas was introduced through a stainless-steel SIKA-R 20 distributor plate of sintered particles with a pore size of 37 μm . An identical distributor plate is placed on the top part of the column to prevent entrainment of any particles outside the column due to elutriation.

Mesoporous γ -alumina, produced by Ketjen as support for hydroprocessing catalysts, was used as the catalyst support. This material has a monomodal pore size distribution containing mesopores, with 90% of the pore volume corresponding to pore size below 12 nm, and no significant amount of macropores. The specific surface area is 271 $\text{m}^2 \text{ g}^{-1}$, estimated by N₂ physisorption. In all experiments the γ -alumina is used as particles at sieve fractions of 125–300 μm , obtained by crushing extrudates, followed by sieving. The precursors used for the deposition of TiO₂ were titanium(IV) isopropoxide 98% (Strem Chemicals) and demineralized water (Veolia). Both precursors were contained in 600 mL stainless-steel bubblers. The bubbler of TTIP was heated at 90 °C while the water bubbler was kept at room temperature. Pressurized N₂ (grade 5.0, Linde Gas) was used as carrier and fluidization gas. In all the experiments the initial mass of Al₂O₃ powder was 3 g, the flow of N₂ was 0.8 l min^{-1} , and the reaction temperature was 180 °C. Before starting the deposition process, the powder was pretreated by heating to the reaction temperature (180 °C) and flushing with N₂ for up to 9 h to remove physisorbed water molecules from the surface.

After the ALD process, the samples were further submitted to a mild calcination at 350 °C to ensure removal of any remaining organics and transformation of titanium hydroxide into the respective oxide. Calcination was carried out in a static oven with a ramp rate of 5 °C min^{-1} and a dwell time of 2 h.

Catalyst characterization

The composition of the coated samples was determined by induced coupled plasma optical emission spectroscopy (ICP-OES) in a Perkin Elmer Optima 3000 DV. Cross-sectional scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDX) was used to determine the

presence of the coating on the inner pore space and the external surface of the particles in a Zeiss EVO MA15-Noran system 7 microscope. Transmission electron microscopy with energy dispersive X-ray spectroscopy (TEM-EDX) was used to assess the dispersion of the deposited TiO_2 overcoat and the CoMo active phase, before and after the catalytic testing. A Tecnai Osiris microscope equipped with a FEG gun was utilized. The porosity characteristics were evaluated by N_2 adsorption using the Brunauer–Emmett–Teller (BET) method in a Quantachrome Autosorb-6B surface area analyser. Alternatively, the surface area of the samples was determined by hexane adsorption using a method³⁴ developed by Ketjen. More details can be found in the ESI.†

Catalytic testing

The coated $\text{TiO}_2\text{--Al}_2\text{O}_3$ support powder was impregnated with a CoMo aqueous-based solution and dried at 120 °C in a static oven (details in ESI†). The metal loadings are comparable to that of commercial catalysts. Subsequently, the catalyst performance was determined under industrially relevant hydroprocessing conditions for the production of ultra-low-sulphur diesel. The catalysts were tested in a fixed bed multi-tubular reactor for hydroprocessing performance testing. Catalysts were tested as particles from crushed extrudates, size-selected in the 125–300 μm range. For all catalysts, 0.9 ml of the catalytic material was measured and loaded in the reactor. The catalysts were sulfided *in situ* with a light gas oil (LGO) feed 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 H_2/LGO ratio of 300 NI l^{-1} . The catalysts were exposed to LGO at 45 bar and a H_2/LGO ratio 300 NI l^{-1} at different feed rates and temperatures, before activity evaluation at 350 °C and a LHSV of 2.0 h^{-1} took place. To assess the effect of the TiO_2 overcoats, catalyst performance of the CoMo/ $\text{TiO}_2\text{--Al}_2\text{O}_3$ catalysts was benchmarked against the performance of a CoMo/ Al_2O_3 catalyst prepared *via* the same preparation method by using the same pristine mesoporous Al_2O_3 as the support. The catalyst performance is expressed as the relative volume activity (RVA) and as the activity per Mo atom (RMA) in hydrodesulphurization (HDS). Further details on the testing procedure can be found in the ESI.†

Results and discussion

Overcoated catalyst support characterization

In our exploratory studies it was found that a satisfactory TTIP exposure time for achieving surface saturation was 90 min. Samples were therefore prepared at 180 °C with 1, 2 and 3 cycles using the dosing times from the calibration study, *i.e.*, 90–120–60–120 min respectively for the exposure of TTIP, purging of TTIP, exposure of H_2O and purging of H_2O . In each run, 3 g of the alumina substrate were coated in the fluidized bed reactor, while the time for pre-treatment was 9 h to ensure extensive removal of physisorbed water. The bulk Ti loading of the samples was quantified using ICP-

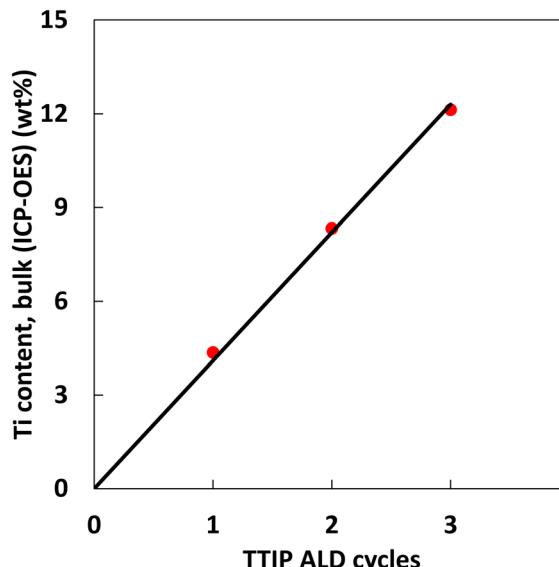
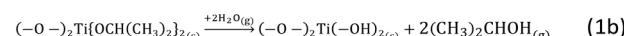


Fig. 1 Titanium content (bulk, measured by ICP-OES) of the samples overcoated with 1, 2 and 3 TTIP ALD cycles. The line indicates a linear fit.

OES, SEM-EDX was used to estimate the Ti-distribution over the cross section of the particles (line scans) and of specific areas (spot analysis), *i.e.*, the centre of cross-sectioned particles.

The Ti loading of the three samples (Fig. 1) increases linearly with the number of ALD cycles. It should be noted that the bulk Ti concentrations estimated from ICP-OES do not give information on the Ti distribution over the particle surface. From the data in Fig. 1 the growth-per-cycle (GPC) can be estimated. The GPC is the ratio of the volume of TiO_2 deposited per cycle and the corresponding surface area. Fig. 1 shows that per cycle *ca.* 4 wt% Ti is deposited, corresponding with *ca.* 7 wt% TiO_2 . The surface area of the alumina used is 271 $\text{m}^2 \text{ g}^{-1}$ and the density of the deposited TiO_2 is assumed to be 3.8 g cm^{-3} . We consider 1 g of product, containing 0.93 g of alumina with a surface area of $271 \times 0.93 \text{ m}^2 \text{ g}^{-1}$ and 0.07 g of TiO_2 with a volume of $0.07/3.8 \text{ cm}^3$. The corresponding GPC equals to 0.07 nm. The value of the GPC is approximately double than the GPC of a comparable ALD process that was estimated for Si wafers by ellipsometry.³¹ For an interpretation of the GPC value it is meaningful to compare it with the GPC value corresponding to a theoretical full coverage of the deposited material, calculated from the stoichiometry of the deposition reaction, taking place as depicted in Scheme 1.³⁵ This scheme shows a stoichiometry of Ti/OH of one to two. For the calculation of a theoretical full coverage with TiO_2



Scheme 1 Simplified interaction of a hydroxylated alumina surface with TTIP and H_2O during the ALD overcoating reactions.

$$\frac{g_{TiO_2}}{g_{product}} = \frac{g_{TiO_2}}{g_{Al_2O_3}} \cdot \frac{1}{\frac{g_{TiO_2}}{g_{Al_2O_3}} + 1} \quad (2)$$

Scheme 2 Conversion of TiO_2 concentration per g of alumina at full coverage, to TiO_2 concentration per g of overcoated catalyst support product.

the concentration of the OH surface groups should be known. The OH concentration of alumina surfaces has been reported in literature.^{36,37} It is a strong function of the pretreatment temperature of the alumina. At the temperature of this study, 180 °C, the OH concentration is 10–12 OH/nm².³⁶ Based on this value, the concentration of TiO_2 for the conditions of the ALD synthesis in this study is estimated to be 5–6 TiO_2 species per nm² alumina. The surface area of the alumina is 271 m² g⁻¹. From these data the TiO_2 concentration per g of alumina at full coverage is calculated to be 1.36×10^{21} to 1.63×10^{21} TiO_2 species per g alumina, corresponding with a TiO_2 content of 18–21.5 wt% on the alumina basis. The value of the mass fraction of TiO_2 per unit mass of product can be calculated according to the relationship depicted in Scheme 2. The resulting value for the theoretical full coverage with TiO_2 is 15–18 wt%.

As shown in Fig. 1 the Ti content after 3 deposition cycles is *ca.* 12 wt%, and thus *ca.* 20 wt% TiO_2 . This number shows that after 3 cycles, the amount of Ti-oxide deposited corresponds to a theoretical full coverage provided that large amounts of 3-D structures are not present. Per cycle *ca.* 2 TiO_2 /nm² are deposited. It should be noted that the GPC value of 0.07 nm is an average over the surface.

SEM-EDX analysis of particle cross-sections was carried out to assess the extent of TiO_2 deposition in the inner pore structure of the particles. A semi-quantitative Ti distribution was obtained. An impression of the Ti distribution inside the TiO_2 – Al_2O_3 particles after 1, 2 and 3 cycles is given in Fig. 2. The Ti concentration increased at increasing number of cycles. In the individual particles the distribution is rather homogeneous with a sharp, relatively concentrated layer of 10–20 μ m at the edges of the particles.

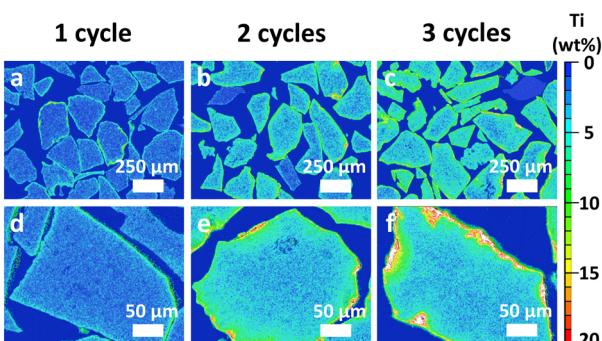


Fig. 2 Titanium distribution (determined by SEM-EDX) inside the TiO_2 – Al_2O_3 particles after 1, 2 and 3 TTIP ALD cycles: (a–c) low and (d–f) high magnifications respectively. White colour indicates a very high (>20 wt%) local Ti content.

For all three samples the concentration differences between particles are rather small. By combining bulk and cross-sectional Ti content measurements, the TiO_2 concentration in the centre of the particles is compared to the bulk composition. Note that in this comparison the amount of Ti is expressed as the wt% of oxides in the total sample, the common way to express composition of hydrotreating catalysts. The TiO_2 concentration in the centre was measured by taking the average of several spot measurements near the centre of 10 different particles (for more details see ESI†).

The obtained line scans (Fig. 3) show the distribution of Ti species along the cross section of the three samples. Except for the aforementioned enrichment in the particle rim, the observed concentration is, in each case, essentially constant over the radial position. This enrichment rim of the particles is in all three cases about the same (*ca.* 20% of the total amount of the TiO_2). Thus, compared to the ideal case of fully homogeneous deposition, roughly 80% of the Ti-oxide is homogeneously distributed over the inner particle surface. As shown in Fig. 4 the content values in the particle centre show close to linear correlation with the bulk concentration. They are roughly 20–30% lower than the bulk concentration.

Despite the homogeneous distribution of the deposited species, coating the inner pores could induce a significant decrease in the specific surface area of the alumina support due to pore blockage. To assess this, the pore size distribution was estimated for one of the samples coated with a single ALD cycle (7.3 wt% TiO_2), using N₂ physisorption (Fig. 5). Similar pore size distributions between the uncoated and coated samples are observed, with a maximum in the pore size distribution curve at the same pore diameter. The delta pore volume (normalized as ml of N₂ adsorbed per g of alumina support) is only slightly larger than expected, based on the density of bulk TiO_2 . It is concluded that the differences between the alumina and the Ti-coated alumina are minor: no extensive pore blocking has taken place.

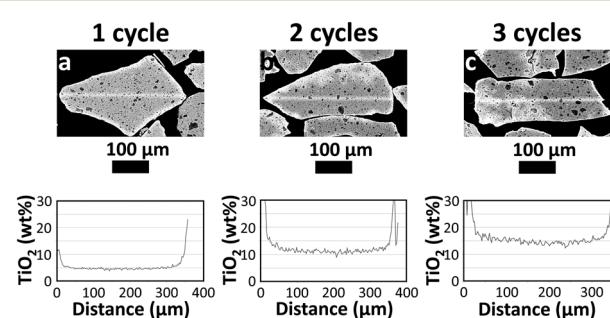


Fig. 3 SEM-EDX line scans showing the TiO_2 distribution along the cross-section of the TiO_2 – Al_2O_3 particles after 1, 2 and 3 TTIP ALD cycles (a, b and c, resp.). The location of the line scan is evident in the images as a brighter line across the length of the selected particle.



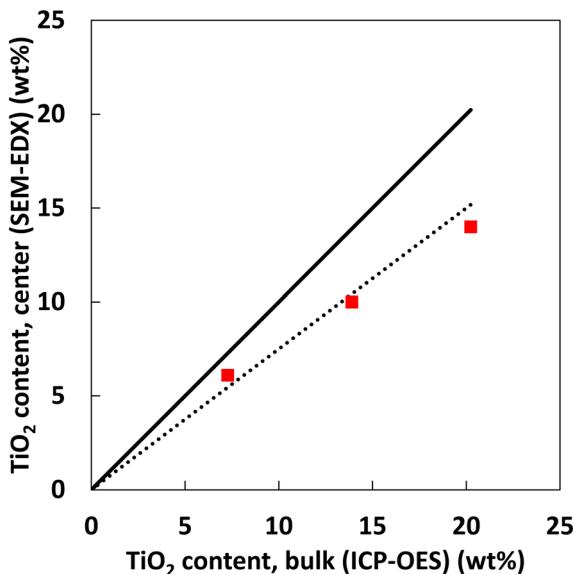


Fig. 4 Correlation of the bulk TiO_2 content (measured by ICP-OES) and the semi-quantitative TiO_2 content near the centre of the particles (determined by SEM-EDX) for samples overcoated with 1, 2 and 3 ALD cycles. The lines are meant to guide the eye and represent 100% parity (solid) and 75% parity (round dot) respectively.

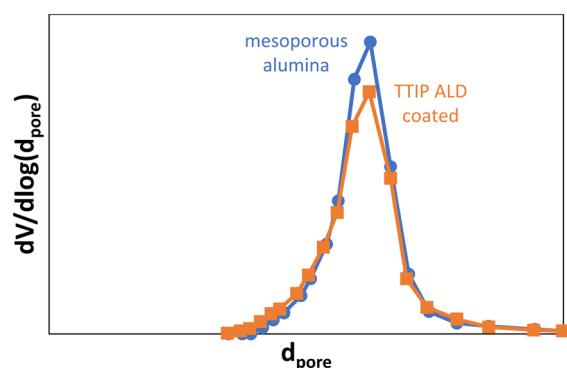


Fig. 5 Pore size distribution (volumetric, normalized) of the uncoated mesoporous alumina support (blue profile, circles) and a single TTIP ALD cycle overcoated sample (orange profile, squares) that contains 7.3 wt% TiO_2 .

The effect of TiO_2 deposition on the surface area of the $\text{Al}_2\text{O}_3\text{-TiO}_2$ materials measured by hexane adsorption (Table 1) confirms that when normalized on γ -alumina (Al_2O_3) basis, no noticeable decrease is observed.

Table 1 Effect of TiO_2 deposition in the surface area of the $\text{TiO}_2\text{-Al}_2\text{O}_3$ materials measured by N_2 physisorption and hexane adsorption

	Alumina base	1 cycle	2 cycles	3 cycles
TiO_2 [wt%]	0	7.3	13.9	20.2
SA-BET [$\text{m}^2 \text{g}^{-1}$]	271	263	— ^a	—
SA-BET [$\text{m}^2 \text{g}_{\text{alumina}}^{-1}$]	271	282	—	—
Hexane ads [$\mu\text{mol g}^{-1}$]	644	578	534	513
Hexane ads [$\mu\text{mol g}_{\text{alumina}}^{-1}$]	644	623	620	643

^a Not measured.

Catalytic activity

The three samples coated by 1, 2 and 3 cycles were used as support for the synthesis of CoMo hydroprocessing catalysts. The HDS catalytic activities of the three coated samples were measured in hydrotreatment of LGO under relevant industrial conditions (350 °C, 45 bar) in a multi-tubular testing unit (for details see ESI†). The HDS activity of the samples is benchmarked against a CoMo/ Al_2O_3 catalyst synthesized directly on the pristine alumina support (Fig. 6).

All the catalysts based on the Ti-coated supports showed significantly higher activity than the reference catalyst. Up to 40% higher relative activity in HDS per Mo atom was obtained for the sample that was modified with 2 ALD overcoat cycles. It is clear that the introduction of the highly dispersed TiO_2 in the catalysts has a beneficial effect on activity, in line with previous reports. We speculate that the observed optimum in activity is related to the dispersion of the Ti species. As the Ti content increases with the number of ALD cycles, approaching the order of a monolayer coating (18–21.5 wt%), the dispersion of the Ti species might be slightly decreasing for the highest Ti loading. Further evaluation of the porosity characteristics for varied Ti contents, and a careful study on the catalyst acidity characteristics and the dispersion of the active phases are expected to enable a better understanding of the reasons behind the increase of the catalytic activity.

Morphology and dispersion of deposited species after the catalyst testing

Besides the distribution and dispersion of the TiO_2 , the morphology of the active CoMoS phase was investigated by TEM (details in ESI†). Imaging of the 7.3 wt% $\text{TiO}_2\text{-Al}_2\text{O}_3$ support and an analogous, spent CoMoS/ $\text{TiO}_2\text{-Al}_2\text{O}_3$ catalyst (Fig. 7) showed, in agreement with the SEM-EDX results, a homogeneous distribution of Ti and Al. At low magnification, the Al and Ti element maps overlap almost perfectly and there are no separate TiO_2 particles observed. At higher magnification, nm-scale Ti oxide particles are observed, evenly distributed and dispersed onto a porous matrix. The obtained images suggest that the TiO_2 deposition has resulted in the formation of very small particles in the range of *ca.* 1 nm in size, distributed homogeneously throughout the pores of the Al_2O_3 without any blockage of the pores. As expected, the Ti and Al distribution for the support and the spent catalyst after the catalytic testing are very similar. This

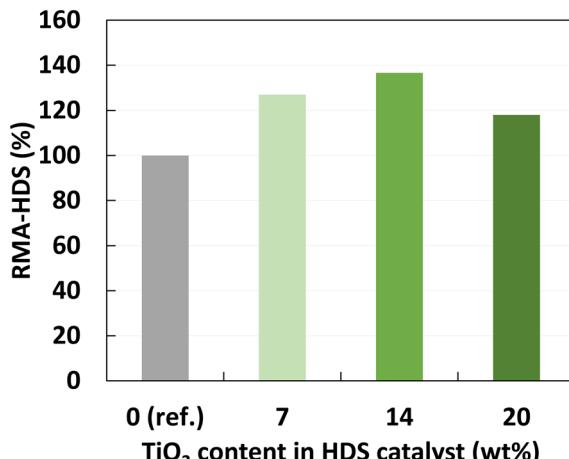


Fig. 6 HDS activity (RMA) of TiO₂-Al₂O₃ supported CoMo catalysts. The Al₂O₃ support was overcoated with 1, 2 and 3 TTIP ALD cycles resulting in 7, 14 and 20 wt% TiO₂ respectively. For benchmarking, the activity of the analogous reference catalyst without a TiO₂ overcoating is included.

similarity indicates that there are no signs of agglomeration during catalyst preparation (impregnation with an aqueous metal solution followed by drying). It is promising that the exposure of the catalyst at the demanding reaction conditions (350 °C, 45 bar) did not seem to influence the dispersion of the TiO₂. Even in samples with a higher Ti loading, the Ti oxide species remained highly dispersed throughout the porous matrix, for both fresh and used samples.

High resolution TEM images of spent catalysts were used to determine the morphology and dispersion of the CoMoS active phase, based on the sample after a single ALD cycle

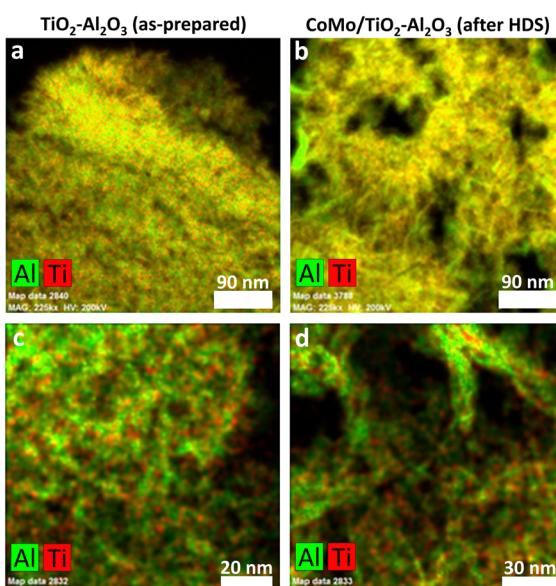


Fig. 7 Distribution of Al and Ti in a representative TiO₂-Al₂O₃ catalyst support (7.3 wt% TiO₂, a and c) and a spent CoMo catalyst supported on the overcoated TiO₂-Al₂O₃ catalyst support (7 wt% TiO₂, b and d) assessed by TEM-EDX. Red: Ti; green Al.

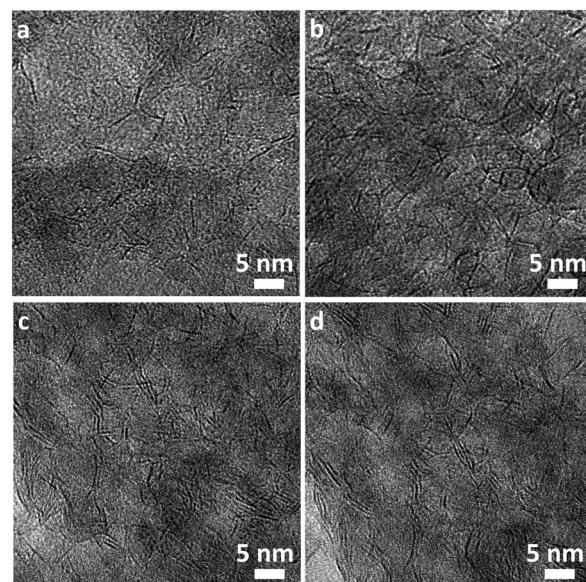


Fig. 8 High resolution TEM images on several sample locations (a-d) of a spent overcoated CoMoS catalyst (7 wt% TiO₂ after 1 TTIP ALD cycle) obtained after the catalytic performance testing.

(7 wt% TiO₂) as shown in Fig. 8. The CoMoS slabs can be observed as black lines, which are in fact projections of the 2-dimensional MoS₂ slabs as observed side-on. Mostly single slabs of 3–7 nm can be observed, but in areas with higher local metal loading, some stacking of the slabs was evident. The slabs positioning seems to follow the contour of the support particles, in agreement with previous visualization *via* 3-dimensional TEM imaging.^{38,39} No noticeable formation of separate cobalt-sulfide particles was observed. Altogether it can be concluded that the introduction of TiO₂ in the support *via* ALD has not resulted in any drastic modification of the active phase. Quantification of the dispersion of the active phase is notoriously difficult due to (i) sample inhomogeneity which makes it difficult to obtain a representative set of images for quantification, (ii) the potential presence of small CoMoS slabs that cannot be traced in the current TEM resolutions (and could contribute to a large amount of active sites), (iii) the large error associated to counting and size measurement of active sites, (iv) the large error associated to counting and size measurement of the observed slabs. As the main objective of this study was to determine the applicability of ALD for the deposition of TiO₂ overcoats in relevant mesoporous catalyst support materials and its positive effect on catalyst activity, we did not attempt any further quantification.

The results strongly suggest that the deposition of TiO₂ did not have a significant effect on the dispersion of the CoMoS phase. We conclude that the positive effect of TiO₂ overcoating on the catalytic performance is not the result of an increased dispersion, in agreement with the suggestion of a modification of the support (a lower support active phase interaction) or of a direct function for titanium sites similar to Ni and Co.^{10,11} A modification of the electronic structure



of the active phase could be the origin,^{5,40} while the TiO₂-surface could also play a role in reaction pathways that facilitate the HDS reaction, such as isomerization of substituted dibenzothiophenes.^{41–43} Determining the exact effect of the TiO₂ overcoat on the activity is beyond the scope of this study.

ALD of TiO₂ onto porous Al₂O₃ supports—such as mesoporous powders typically used in catalysis applications—has already been showcased in the 1990s pioneering ALD research collaboration of Microchemistry and Neste.^{23–28} Further research^{30,31,44} has proven the benefits of ultrathin coatings in catalytic applications. This is the first report that presents extensive evidence on the intra-particle and inter-particle distribution of the Ti-oxide overcoat. A clear performance benefit, under industrially-relevant conditions, is observed and attributed to the overcoat.

Conclusions

The feasibility of titanium tetra-isopropoxide as ALD precursor for the synthesis of mesoporous TiO₂–Al₂O₃ with high homogeneity on the intra-particle and inter-particle levels was demonstrated. The overcoated TiO₂–Al₂O₃ is an excellent support for the synthesis of a hydroprocessing catalyst with respect to catalytic activity and structural stability of the active phase, although long-term stability remains to be proven. Under reaction conditions, an evenly distributed coating of TiO₂ is present. ALD is a simple and scalable method that allows solvent-free synthesis of precisely-defined structured catalyst supports.

Author contributions

Jacob A. Moulijn: conceptualization, supervision, writing. J. Ruud van Ommen: conceptualization, methodology. Aristeidis Goulas: conceptualization, formal analysis, investigation, methodology, writing. David Valdesueiro: formal analysis, investigation. Jana Juan-Alcañiz: conceptualization, investigation. Kar-Ming Au-Yeung: investigation. Leo Woning: formal analysis, investigation. Jaap A. Bergwerff: conceptualization, supervision, writing.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 H. Topsøe, B. S. Clausen and F. E. Massoth, in *Catalysis-Science and Technology*, ed. J. R. Anderson and M. Boudart, Springer, Berlin, Heidelberg, 1996, vol. 11.

- 2 H. Toulhoat and P. Raybaud, *Catalysis by transition metal sulphides : from molecular theory to industrial application*, Editions Technip, Paris, France, 2013.
- 3 S. Eijsbouts, *Appl. Catal., A*, 1997, **158**, 53–92.
- 4 H. Shimada, *Catal. Today*, 2003, **86**, 17–29.
- 5 M. Breysse, P. Afanasiev, C. Geantet and M. Vrinat, *Catal. Today*, 2003, **86**, 5–16.
- 6 G. M. Dhar, B. N. Srinivas, M. S. Rana, M. Kumar and S. K. Maity, *Catal. Today*, 2003, **86**, 45–60.
- 7 W. Zhou, L. Yang, L. Liu, Z. Chen, A. Zhou, Y. Zhang, X. He, F. Shi and Z. Zhao, *Appl. Catal., B*, 2020, **268**, 118428.
- 8 S. K. Maity, J. Ancheyta, M. S. Rana and P. Rayo, *Energy Fuels*, 2006, **20**, 427–431.
- 9 J. Ramirez, L. Ruiz-Ramirez, L. Cedeno, V. Harle, M. Vrinat and M. Breysse, *Appl. Catal., A*, 1993, **93**, 163–180.
- 10 C. Arrouvel, M. Breysse, H. Toulhoat and P. Raybaud, *J. Catal.*, 2005, **232**, 161–178.
- 11 L. Coulier, J. A. R. van Veen and J. W. Niemantsverdriet, *Catal. Lett.*, 2002, **79**, 149–155.
- 12 E. Y. Kaneko, S. H. Pulcinelli, V. Teixeira da Silva and C. V. Santilli, *Appl. Catal., A*, 2002, **235**, 71–78.
- 13 B. J. O'Neill, D. H. K. Jackson, J. Lee, C. Canlas, P. C. Stair, C. L. Marshall, J. W. Elam, T. F. Kuech, J. A. Dumesic and G. W. Huber, *ACS Catal.*, 2015, **5**, 1804–1825.
- 14 C. Detavernier, J. Dendooven, S. Pulinthanathu Sree, K. F. Ludwig and J. A. Martens, *Chem. Soc. Rev.*, 2011, **40**, 5242–5253.
- 15 J. R. van Ommen, A. Goulas and R. L. Puurunen, in *Kirk-Othmer Encyclopedia of Chemical Technology*, 2022.
- 16 J. Lu, J. W. Elam and P. C. Stair, *Acc. Chem. Res.*, 2013, **46**, 1806–1815.
- 17 J. R. van Ommen and A. Goulas, *Mater. Today Chem.*, 2019, **14**, 100183.
- 18 Y. J. Pagán-Torres, J. Lu, E. Nikolla and A. C. Alba-Rubio, in *Studies in Surface Science and Catalysis*, ed. P. Fornasiero and M. Cargnello, Elsevier, 2017, vol. 177, pp. 643–676.
- 19 J. V. Muntean, J. A. Libera, S. W. Snyder, T. Wu and D. C. Cronauer, *Energy Fuels*, 2013, **27**, 133–137.
- 20 W. W. McNeary, S. A. Tacey, G. D. Lahti, D. R. Conklin, K. A. Unocic, E. C. D. Tan, E. C. Wegener, T. E. Erden, S. Moulton, C. Gump, J. Burger, M. B. Griffin, C. A. Farberow, M. J. Watson, L. Tuxworth, K. M. Van Allsburg, A. A. Dameron, K. Buechler and D. R. Vardon, *ACS Catal.*, 2021, **11**, 8538–8549.
- 21 S. Said and A. A. Abdelrahman, *J. Sol-Gel Sci. Technol.*, 2020, **95**, 308–320.
- 22 A. Goulas and J. R. van Ommen, *Kona Powder Part. J.*, 2014, **31**, 234–246.
- 23 E. L. Lakomaa, S. Haukka and T. Suntola, *Appl. Surf. Sci.*, 1992, **60–61**, 742–748.
- 24 S. Haukka, E. L. Lakomaa and T. Suntola, *Thin Solid Films*, 1993, **225**, 280–283.
- 25 S. Haukka, E. L. Lakomaa, O. Jylha, J. Vilhunen and S. Hornytzkyj, *Langmuir*, 1993, **9**, 3497–3506.
- 26 E.-L. Lakomaa, *Appl. Surf. Sci.*, 1994, **75**, 185–196.
- 27 S. Haukka, A. Kytökivi, E. L. Lakomaa, U. Lehtovirta, M. Lindblad, V. Lujala and T. Suntola, in *Studies in Surface*



Science and Catalysis, ed. G. Poncelet, J. Martens, B. Delmon, P. A. Jacobs and P. Grange, Elsevier, Louvain-La-Neuve, 1995, vol. 91, pp. 957–966.

28 M. Lindblad, S. Haukka, A. Kytökivi, E.-L. Lakomaa, A. Rautiainen and T. Suntola, *Appl. Surf. Sci.*, 1997, **121**–122, 286–291.

29 J. Keränen, C. Guimon, E. Iiskola, A. Auroux and L. Niinistö, *Catal. Today*, 2003, **78**, 149–157.

30 J. Lu, K. M. Kosuda, R. P. Van Duyne and P. C. Stair, *J. Phys. Chem. C*, 2009, **113**, 12412–12418.

31 N. Yang and S. F. Bent, *J. Catal.*, 2017, **351**, 49–58.

32 J.-P. Niemelä, G. Marin and M. Karppinen, *Semicond. Sci. Technol.*, 2017, **32**, 093005.

33 A. P. Didden, J. Middelkoop, W. F. A. Besling, D. E. Nanu and R. V. D. Krol, *Rev. Sci. Instrum.*, 2014, **85**, 013905.

34 J. N. Louwen and R. J. Jonker, Method of analyzing microporous material, US2002/0110921A1, 2002.

35 A. M. Johnson and P. C. Stair, *J. Phys. Chem. C*, 2014, **118**, 29361–29369.

36 H. Knözinger and P. Ratnasamy, *Catal. Rev.: Sci. Eng.*, 1978, **17**, 31–70.

37 M. Digne, P. Sautet, P. Raybaud, P. Euzen and H. Toulhoat, *J. Catal.*, 2002, **211**, 1–5.

38 S. Eijsbouts, X. Li, J. Juan-Alcaniz, L. C. A. van den Oetelaar, J. A. Bergwerff, J. Loos, A. Carlsson and E. T. C. Vogt, *ACS Catal.*, 2017, **7**, 4817–4821.

39 K. P. de Jong, L. C. A. van den Oetelaar, E. T. C. Vogt, S. Eijsbouts, A. J. Koster, H. Friedrich and P. E. de Jongh, *J. Phys. Chem. B*, 2006, **110**, 10209–10212.

40 R. Burch and A. Collins, *J. Catal.*, 1986, **97**, 385–389.

41 S. A. Giraldo and A. Centeno, *Catal. Today*, 2008, **133**–135, 255–260.

42 T. Isoda, S. Nagao, X. Ma, Y. Korai and I. Mochida, *Energy Fuels*, 1996, **10**, 1078–1082.

43 M. V. Landau, D. Berger and M. Herskowitz, *J. Catal.*, 1996, **159**, 236–245.

44 R. Lobo, C. L. Marshall, P. J. Dietrich, F. H. Ribeiro, C. Akatay, E. A. Stach, A. Mane, Y. Lei, J. Elam and J. T. Miller, *ACS Catal.*, 2012, **2**, 2316–2326.

