

Electronic Supplementary Information

New Insights on Oxidative Desulfurization for Low Sulfur Residual Oil Production

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Section 1: Instrumentation and Experimental Details

(A) Characterizations:

Commercially available extruded γ - Al_2O_3 (surface area $>250 \text{ m}^2/\text{g}$) was used as the support material. Analytical grade 30% hydrogen peroxide, tertiary butyl hydrogen peroxide (TBHP) solution, cumene hydroperoxide (CHP) solution, ammonium heptamolybdate, ammonium metatungstate, ammonium metavanadate, oxalic acid, methanol was purchased from Sigma Aldrich and used as received. Powder X-ray diffraction (PXRD) patterns were recorded on Phillips PANalytical diffractometer for Cu $K\alpha$ radiation ($\alpha = 1.5406 \text{ \AA}$), with a scan speed of 1° min^{-1} and a step size of 0.02° in 2θ and Rigaku MicroMax 007HF diffractometer. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Optics ALPHA-E spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory in the $400\text{--}4000 \text{ cm}^{-1}$. Thermogravimetric analyses (TGA) were carried out on a TG50 analyzer (Mettler-Toledo) under N_2 atmosphere with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. BET surface of the samples were measured using Micromeritics instrument. Prior to surface area analysis the samples were activated at $130 \text{ }^\circ\text{C}$ for 8h. SEM images were recorded on FEI Quanta 450 FEG scanning electron microscope with tungsten filament as electron source operated at 10 kV. ICP-MS analysis was carried out on Agilent 7800. GC-SCD/ GC-MS analysis of the sample was carried out on Agilent Technologies (7890B) instrument while kinetic study using model compound was established using UV-Vis spectrophotometer (Schimadzu 2600). TS/TN analysis of the feed and desulfurized sample was measured in Antek by PAC (16-308). CCR% of the sample was determined using Automated Carbon Residue Tester (Tanaka Scientific Ltd., ACR-M3). TAN value of the feed and desulfurized sample was measured using automated potentiometric titrator (Metrohm AG, 905 Tritando). Meanwhile pour point of the sample was determined using pour point apparatus (Instrumentation Scientifique de Laboratoire by PAC, MPP 5G2S/V22402). Recycling of CHP was carried out on vacuum distillation apparatus (ASTM D-1160) (D1160CC/S).

(B) Experimental Procedure:

(i) Kinetic study using model compound: Kinetic study with residual oil feed was further verified by using a model compound: dibenzothiophene (DBT). DBT standard solution was prepared by dissolving 15 mg of DBT in 250 mL of heptane. In a 500 mL 2-neck round bottom flask, 100 mL of this standard solution was taken. To it 5g of $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalyst, 30 (v/v)% of CHP and 100 mL of acetonitrile was added. The resultant reaction mixture was gradually heated to 80°C under constant stirring. 4 mL of aliquot was taken out every time from the heptane phase after the desired time interval and was subjected to UV-Vis measurement. Two set of reactions were carried out, one at 80°C (S1) and other at 60°C (S2).

(ii) Determination of V_2O_5 loading on Al_2O_3 : About 5.89 mg of the catalyst sample was accurately weighed out, to it 10 mL of 40% aqua regia was added. The resultant solution was subjected to digestion

at 90°C followed by dilution to 50 times. Subsequently vanadium standard solution of 0.01 ppm, 0.05 ppm, 0.1 ppm, 0.5 ppm, 1 ppm and 2 ppm were prepared for calibration curve. Loading of V₂O₅ was evaluated following the standard calibration curve.

(C) Measurement of desulfurized oil properties:

(i) Estimation of total sulfur content: Total sulfur content in the feed and treated oil was estimated using ASTM D5453. ASTM D5453 is an established test method for the determination of total sulfur in liquid hydrocarbons by combustion and subsequent detection under UV fluorescence. In brief, the liquid sample was directly injected by a fully automated liquid sampler, into a high temperature combustion tube. Sulfur components present in the samples were vaporized and combusted to sulfur dioxide (SO₂) in an oxygen rich atmosphere. An inert gas stream (helium) carried the reaction products (SO₂) to a UV chamber, where in the SO₂ molecules were excited via absorption of UV light. While relaxing of the excited molecules, the emitted signal was measured by photomultiplier tube. The response signal was integrated to calculate the area. The total sulfur concentration present in the feed and treated product was calculated using a calibrated standard.

(ii) Determination of CCR: CCR content of the feed and treated sample was measured following ASTM D4530. In brief, empty sample vials were placed in an oven for conditioning, followed by cooling it in a desiccator. Empty vials were weighed, followed by addition of desired sample of specific weight. The vials were placed into the oven chamber when the temperature was below 100°C, and the lid was secured. The placed sample was heated up to 500°C under the flow of nitrogen. After attaining 500°C, the sample was allowed to cool down. Once ambient temperature was attained, the vials were taken out of the chamber with the help of sample holder and placed inside a desiccator prior weighing. Finally, the sample weight was measured, and CCR% was evaluated following the equation: $CCR (\%) = [(weight\ of\ vial\ after\ heating - empty\ vial\ weight) / actual\ weight\ of\ sample] * 100$.

(iii) Determination of pour point: Pour point of the feed and treated sample was measured following ASTM D97. In brief, about 0.5 mL of the sample was injected in a test vial using micro-pipette. Special care must be taken care to avoid bubbles, stain etc. inside the vial. The vial was closed with the specified stopper and placed inside the detection chamber of the instrument (MPP 5G2S/V22402). The lid of the chamber was kept closed and pour point value was automatically evaluated following automated programming set up of the instrument.

(iv) Determination of TAN: Total acid number (TAN) of the feed and treated sample was measured following ASTM D664. In brief, tubing of the exchange unit and the dosing unit was rinsed and kept bubble free. The desired sample was weighed in the beaker and titration solvent was added to it. The beaker was then placed on the stirrer, electrode and dosing tube was immersed on to it. Once the sample was dissolved completely, automated titration was carried out. Completion of the titration yielded the TAN of the respective samples.

Section 2: Homogeneous Catalysis

Table T1. Miscibility of refinery grade residual oil with different solvents.

Sl. No.	Solvent combination	Boiling Point (°C)	Ratio	Condition	Result
1	PEG	290	1:1	RT	Phase separation
2	Ethanol	78	1:1	RT	Phase separation
3	Ethanol	78	1:1	60 °C	Phase separation
4	ACN	82	1:1	RT	Phase separation
5	ACN	82	1:1	60 °C	Phase separation
6	Acetone	56	1:1	RT	No phase separation
7	TEG	275	1:1	RT	No phase separation
8	Water	100	1:1	RT	Phase separation
9	NMP	202	1:1	RT	No phase separation
10	Methanol	65	1:1	RT	Phase separation
11	Methanol-NMP	-	1:1	RT	No phase separation
12	Methanol-ACN	-	1:1	RT	Phase separation

It is evident from the Table, that acetone, TEG, NMP could not be used as extractant (with no phase separation). In contrast, methanol and acetonitrile being the low boiling solvents in the series could be used for extraction purpose. Methanol having the lowest boiling point is used for next set of reactions owing to phase separation property and easy recyclability. In addition, at least 1:1 feed to solvent ratio is required to be maintained for phase separation.

Table T2. ODS reactions in presence of homogeneous catalysts.

Sr. No.	H ₂ O ₂ (v/v%)	Acid (v/v%)	Extractant Used (1:1)	Sulfur Reduction (%)
Acid: Acetic Acid				
1	10%	3%	ACN	23.2
2	10%	10%	ACN	28.0
3	15%	30%	Methanol	40.5
4	30%	30%	Methanol	75.5
Acid: Formic Acid				
5	20%	20%	ACN	55.02
6	20%	30%	ACN	66.67
7	30%	20%	Methanol	53.33
8	30%	30%	Methanol	86.01

Section 3: Brief Literature Review

Table T3. Summary of literatures (patents) which demonstrated ODS process for desulfurization of heavy fuel oil.

Type of Oil	Catalyst	Oxidant	Conditions	S reduction %	Sulfone removal	Company
Heavy oil (2%)	$K_2O-Fe_2O_3$ (Ferrites)	-----	390-450 °C, 14-100 bar	63%	-----	Shell
Residue oil (3-4%)	Acetic acid/ $NaIO_4$	H_2O_2 , H_2SO_4 , BaO_2	80°C	60-80%	Molten NaOH treatment	ExxonMobil
Heavy oil (2.6%)	Oxohydroxy-bis-(8-hydroxyquinoline) vanadium	O_3	RT (19°C)	45%	Heating at 350 °C	Texaco Inc
Heavy oil (2.5%)	$MoO_3-Al_2O_3$	TBHP	100°C	35-40%	Heating at 320 °C with $NaO_2-Al_2O_3$	Texaco Inc
VGO (3.25%)	bis(glycerol)oxotitanium(IV)	H_2O_2	60°C	70%	Solvent extraction	Auterra
Gas oil (2%)	MoO_3 (ZrO_2 , V_2O_5)	TBHP	100°C	99%	Adsorption in SiO_2 column	Institut Francais Du Petrole
Gas oil	Dodecamolybdophosphoric Acid, Molybdotungstic Phosphonate etc.	H_2O_2	80-100°C	95%	Solvent extraction/ phase separation	SABIC

Although a lot of efforts have been devoted for ODS reaction, but the desulfurization efficiency is often lower. Meanwhile when TBHP is used the desulfurization is enhanced, but its recycling appears to be a difficult task.

Section 4: Characterizations

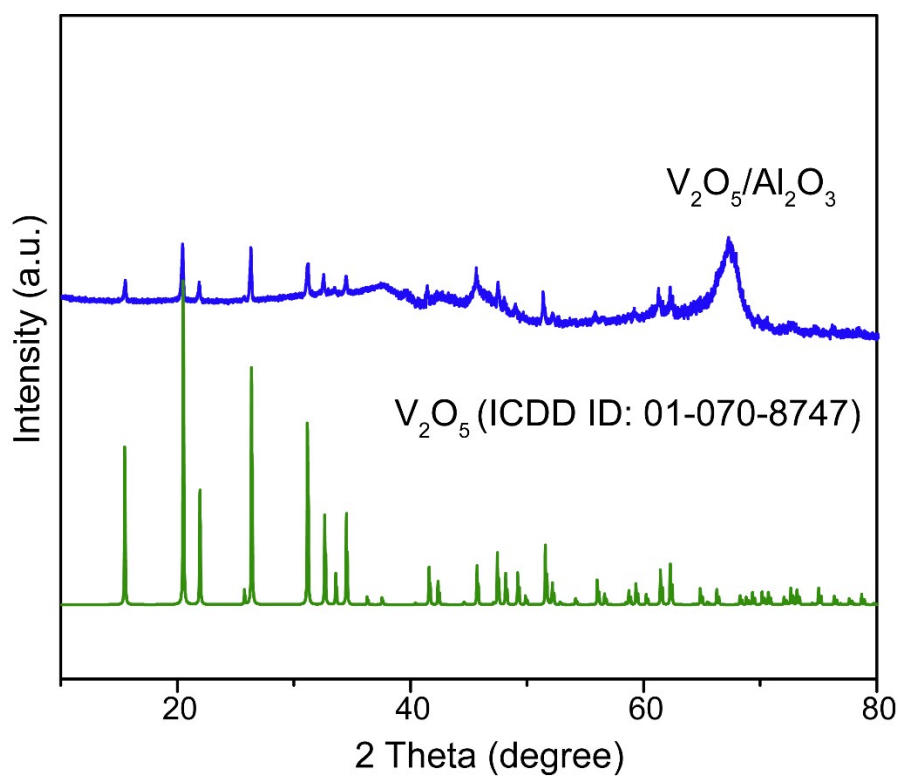


Figure S1. PXRD pattern of V_2O_5/Al_2O_3 which shows crystalline phase of V_2O_5 [ICDD ID: 01-070-8747].

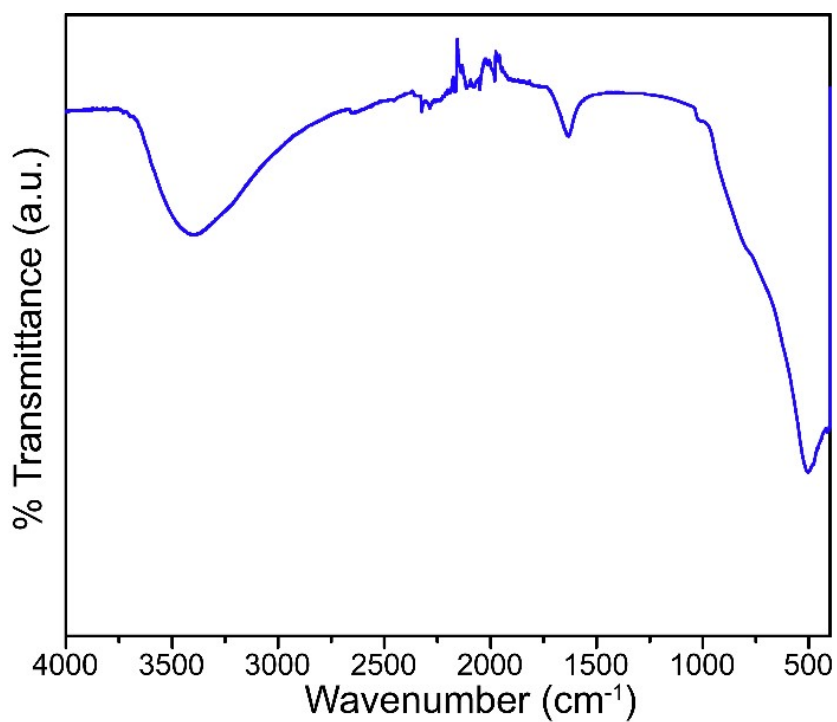


Figure S2. FTIR spectra of V_2O_5/Al_2O_3 , where V=O and V-O-V stretching of V_2O_5 loaded on to Al_2O_3 was observed at 1019 cm^{-1} and 505 cm^{-1} respectively.

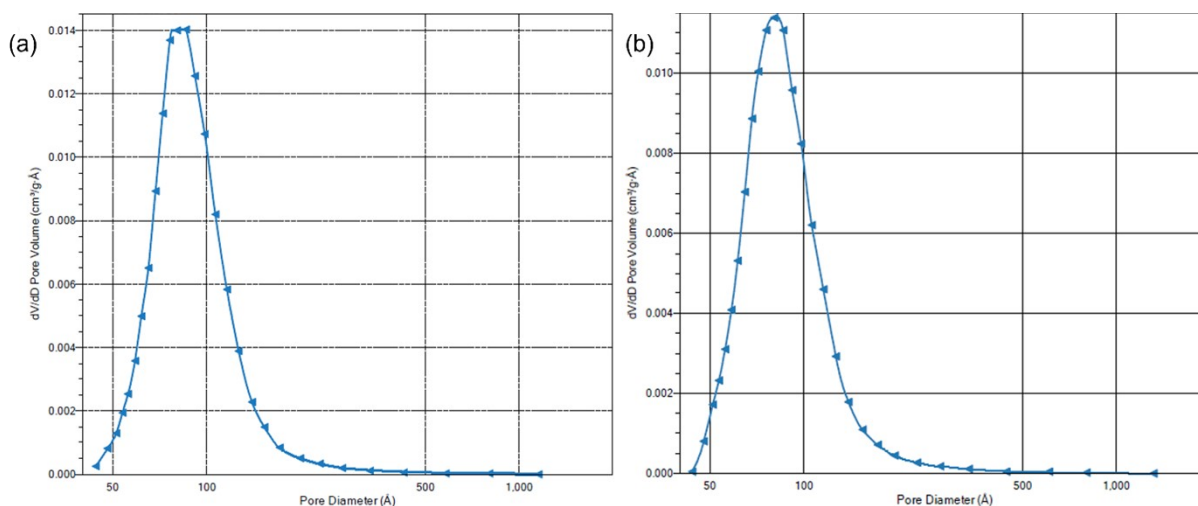


Figure S3. BJH pore size analysis of (a) Al_2O_3 and (b) $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$. Pore diameter of Al_2O_3 and $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ was measured to be 9.6 nm and 9.45 nm respectively.

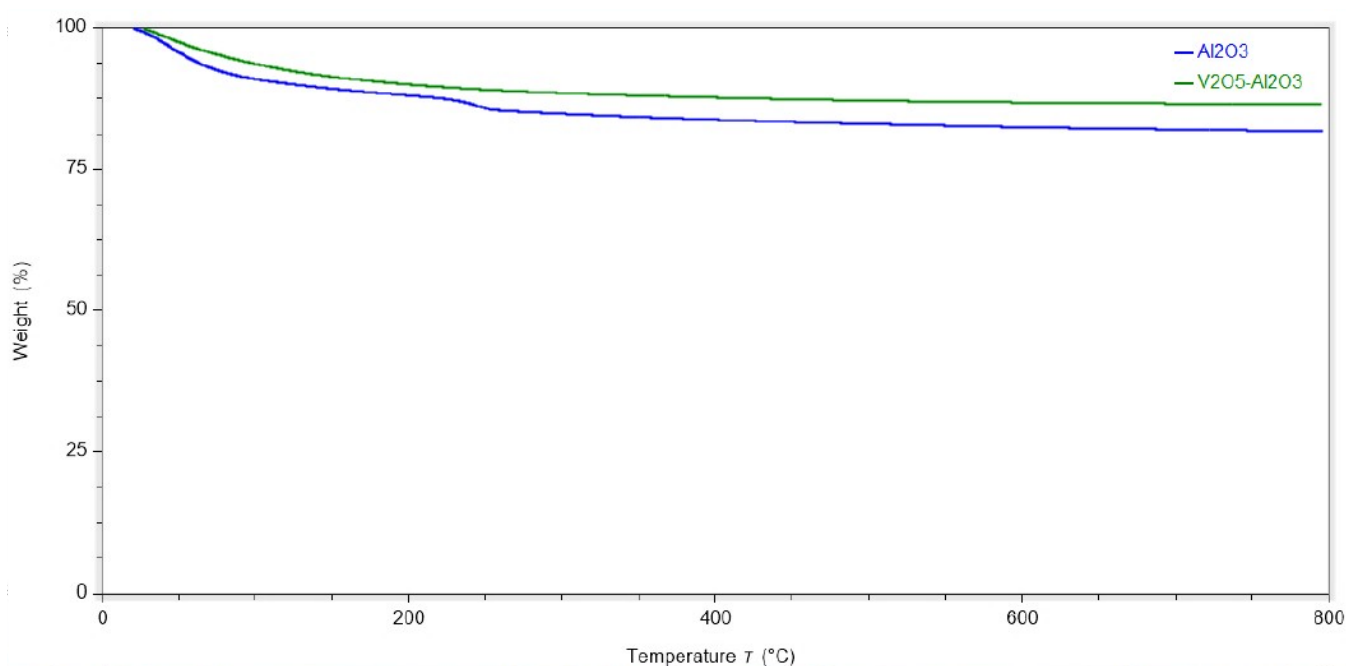


Figure S4. TGA analysis of Al_2O_3 and $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ respectively. TGA analysis signified that $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ is stable up to 800°C with only $\sim 13\%$ weight loss observed. Amongst them $\sim 9\%$ weight loss up to 150°C signified the removal of moisture and dead sorbed water molecules from the surface of the catalyst.

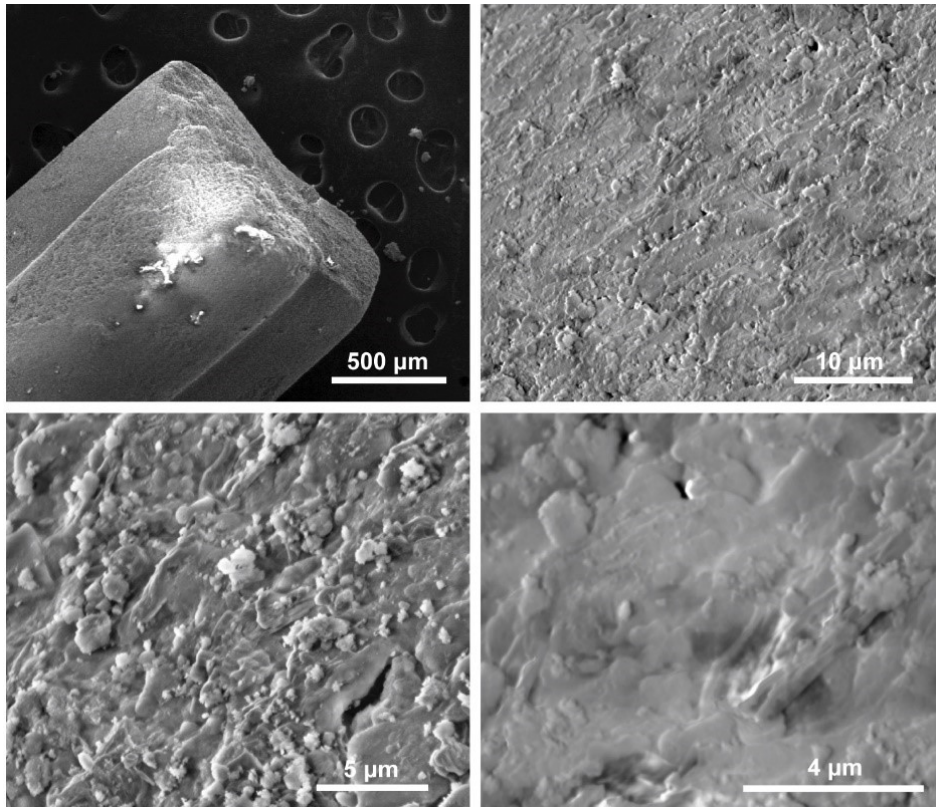


Figure S5. SEM images of Al₂O₃. SEM image demonstrated smooth surface of Al₂O₃ which was distinctly different from V₂O₅/Al₂O₃ shown below.

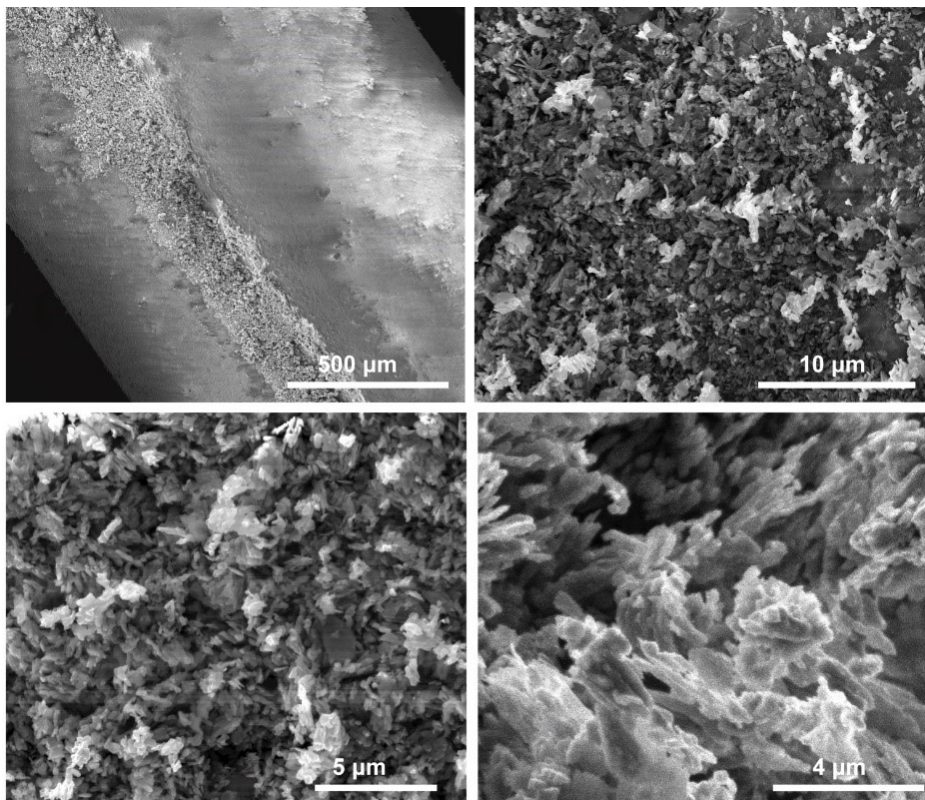


Figure S6. SEM images of V₂O₅/Al₂O₃. SEM image demonstrated deposition of rod shaped V₂O₅ on to the surface of Al₂O₃ after wet impregnation and calcination method.

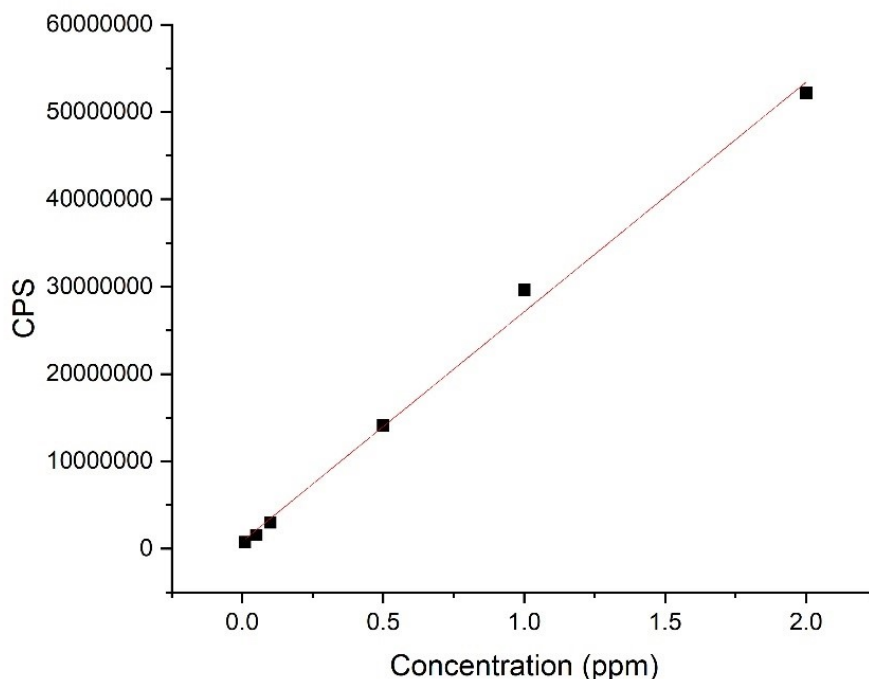


Figure S7. Calibration curve of vanadium standard to determine the concentration of vanadium loaded on to Al_2O_3 . About 5.69 mg of catalyst sample was digested in 10 mL of 40% aqua regia followed by dilution to 50 times. Standard calibration solution of vanadium was prepared with concentration of 0.01 ppm, 0.05 ppm, 0.1 ppm, 0.5 ppm, 1 ppm and 2 ppm respectively. Based on the prepared calibration curve, the concentration of the stock solution was found to be 31.9 ppm which correlated to 10 wt.% loading of V_2O_5 on to Al_2O_3 .

Section 5: Heterogeneous Catalysis

Table T4. Effect of desulfurization on ODS using different amount of (a) $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$, (b) CHP, and (c) pressure. Methanol was used as the extracting solvent in each reaction and total sulfur content was estimated after phase separation of methanol using TS/TN analysis (ASTM D5453).

Sr. No.	Oxidant (CHP)	Temp. (°C)	Catalyst ($\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$)	Pressure (bar)	Desulfurization (%)
1	30 (v/v)%	80	5 wt.%	1	73.2%
2	30 (v/v)%	80	2.5 wt.%	1	62.5%
3	20 (v/v)%	80	5 wt.%	1	66.1%
4	20 (v/v)%	80	2.5 wt.%	1	53.8%
5	30 (v/v)%	80	5 wt.%	6	73.8%

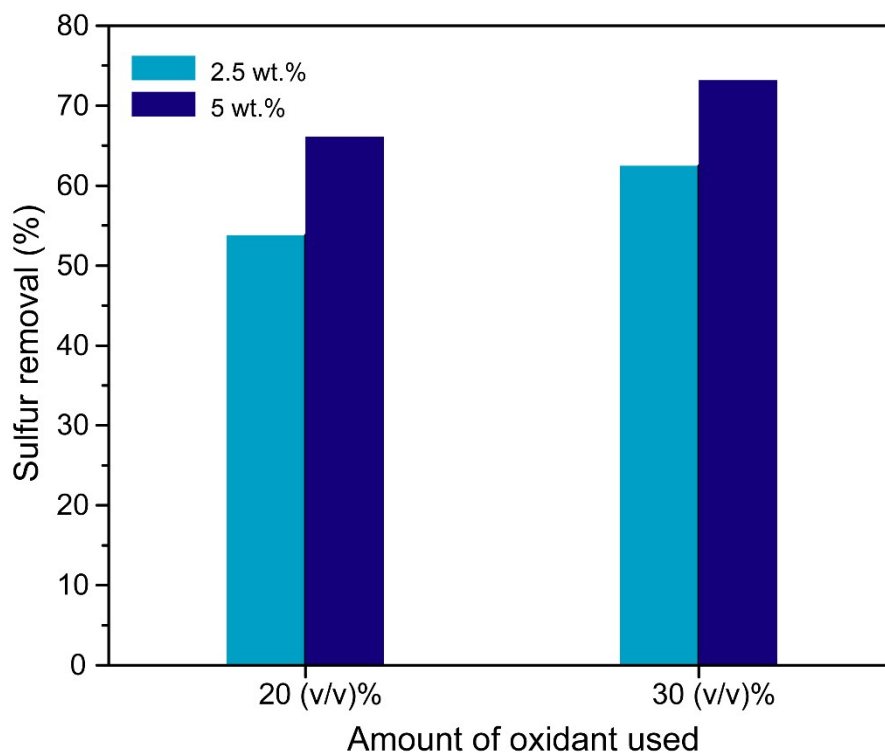


Figure S8. Comparison of desulfurization of residual oil feed using two different amount catalyst. 5 wt.% of catalyst demonstrated greater desulfurization.

Table T5. ODS reaction using different heterogeneous catalyst (5 wt.%), 30 (v/v)% of CHP at 80°C, and subsequent degree of desulfurization. Methanol was used as the extracting solvent in each reaction and total sulfur content was estimated after phase separation of methanol using TS/TN analysis (ASTM D5453).

Sr. No.	Heterogeneous Catalyst (5 wt.%)	Desulfurization (%)
1	Ti-silicate	12.2%
2	MoO ₃ /Al ₂ O ₃	40.33%
3	WO ₃ /Al ₂ O ₃	42%
4	WO ₃ /Ti-silicate	14.7%
5	MoO ₃ -WO ₃ /Al ₂ O ₃	47.25%
6	V ₂ O ₅ /TiO ₂	61.1%
7	V ₂ O ₅ /Al ₂ O ₃	73.2%

Section 6: Kinetics and Mechanism

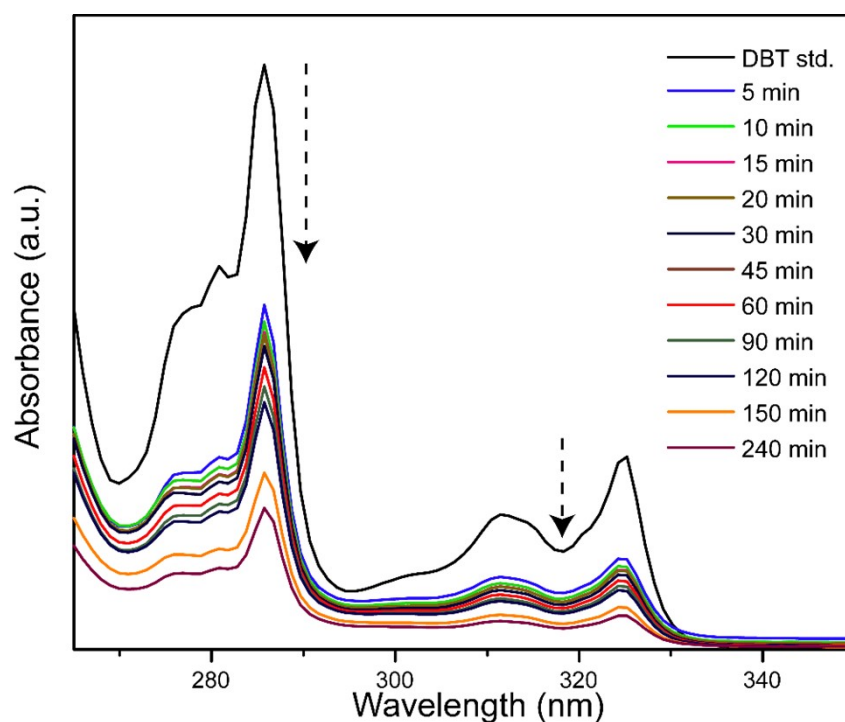


Figure S9. Kinetic study of ODS reaction with DBT as the model compound, using 5 wt.% of V_2O_5/Al_2O_3 catalyst, 30 (v/v)% of CHP at 80°C (1 bar) (Set S1). Aliquots were taken out after certain time intervals and were subjected to UV-Vis analysis. Concentration of DBT was continuously decreased as the reaction progressed.

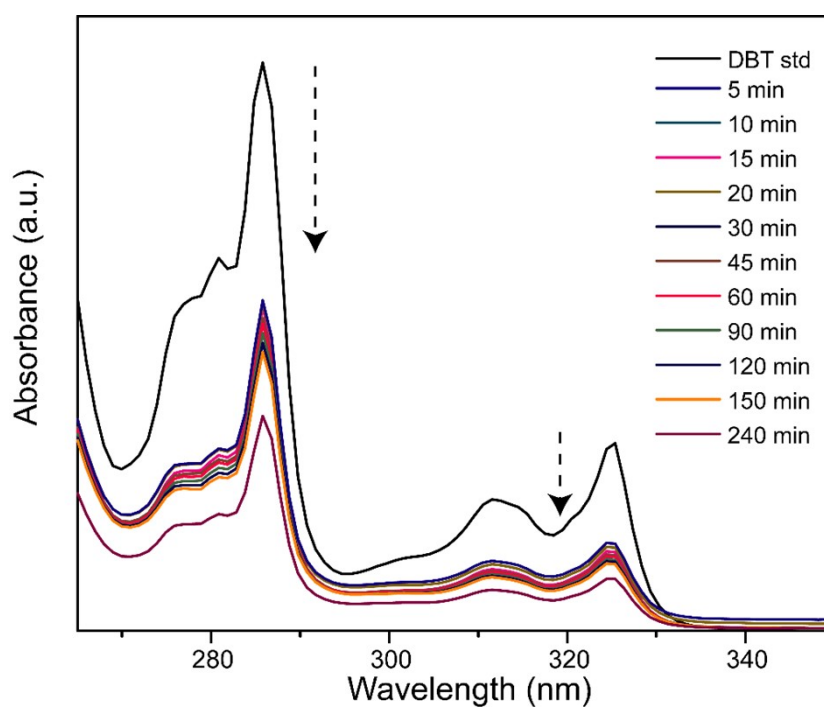


Figure S10. Kinetic study of ODS reaction with DBT as the model compound, using 5 wt.% of V_2O_5/Al_2O_3 catalyst, 30 (v/v)% of CHP at 60°C (1 bar) (Set S2). Aliquots were taken out after certain time intervals and were subjected to UV-Vis. Concentration of DBT was decreased continuously.

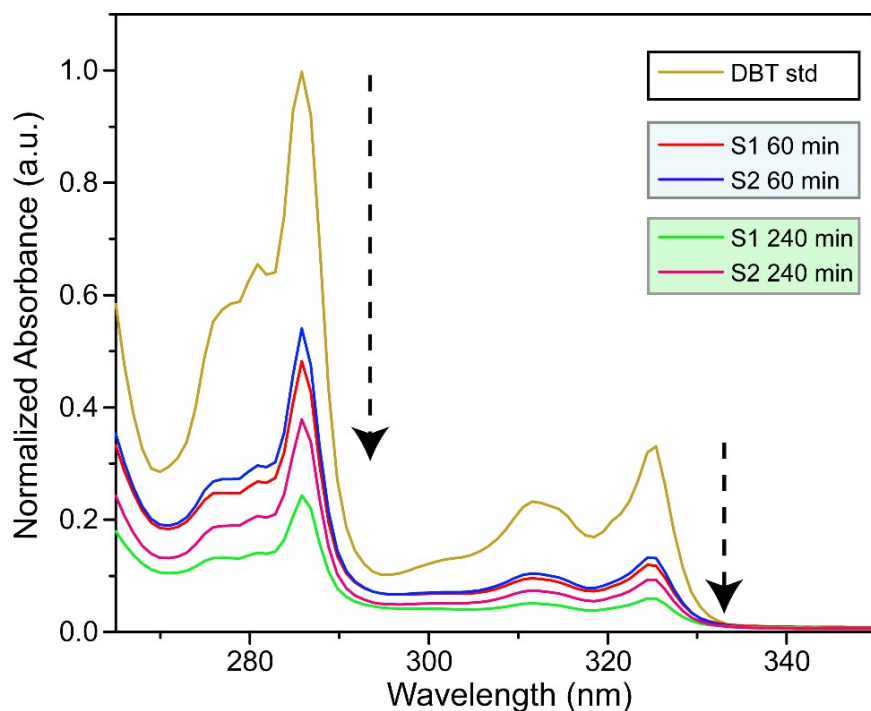


Figure S11. Comparison of kinetic study between S1 and S2. S1 being carried out at a higher temperature demonstrated faster DBT removal kinetics compared to S2.

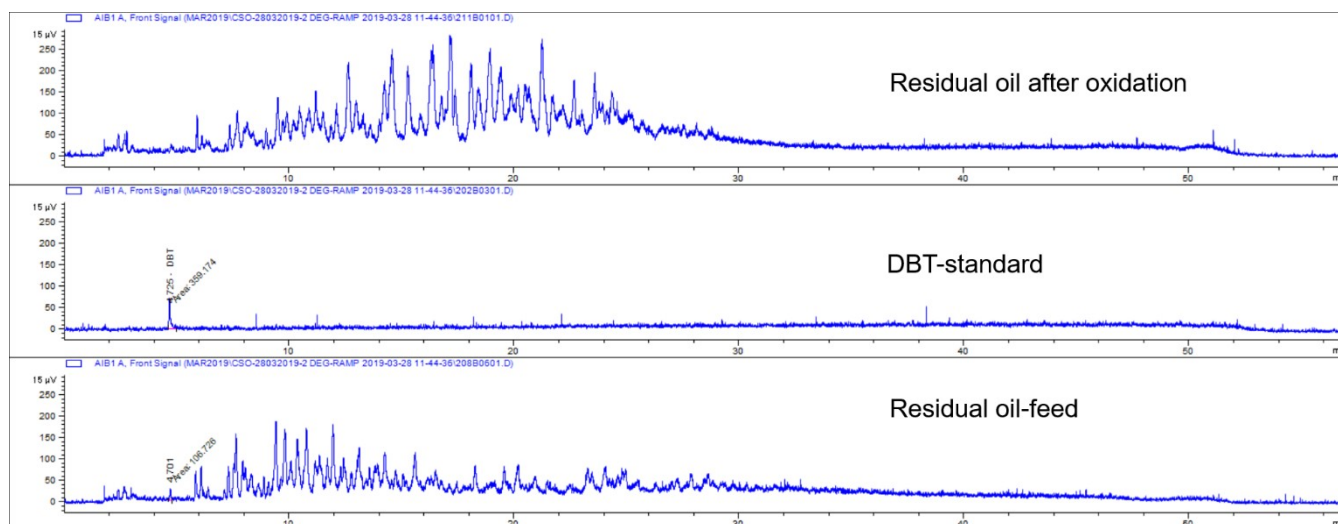


Figure S12. GC-SCD analysis of residual oil feed, treated residual oil (residual oil after oxidation) and DBT-standard. GC-SCD analysis confirms that dibenzothiophenes are converted to sulfones after reaction.

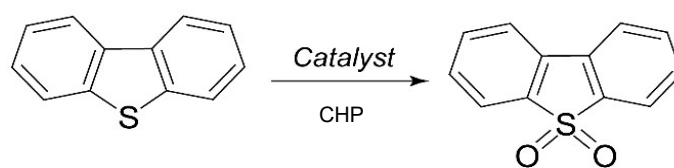


Figure S13. ODS reaction with model compound to check the CCR content after oxidation.

Table T6. Measurement of CCR content of the reaction mixture using ODS heterogeneous catalysis system and DBT as model compound.

Sample Name	CCR %
DBT pure in toluene (1 wt%)	0.01
DBT pure after reaction	0.06
DBT pure in toluene (2 wt%)	0.00
DBT pure after reaction	0.01
DBT-sulfone pure in toluene	0.00

Section 7: Technoeconomic Evaluation

Table T7. Technoeconomic evaluation of ODS process using 5 wt.% V₂O₅/Al₂O₃ as catalyst, 30 (v/v) % CHP as oxidant and methanol as extractant.

Sr. No.	Parameters	UOM		Remarks
1.	Raw Material Cost	\$/T of product	647	
1a	Feed cost	\$/T of product	350	Refinery grade residual oil is typically available at USD 300-320
1b	Catalyst cost (V ₂ O ₅ /Al ₂ O ₃)	\$/T of product	75	V ₂ O ₅ cost USD 13/ kg. 10 wt.% of V ₂ O ₅ loading for 5 wt.% catalyst with at least 5 cycles of regeneration. Alumina is available at USD 8/Kg
1c	Solvent cost (Methanol)	\$/T of product	22	95% solvent is recyclable, 5% of handling loss.
1d	Oxidant cost	\$/T of product	200	80% of CHP is recyclable with 80% of regeneration yield. Top up amount is 36%. (Price: USD 1.6/kg)
2.	Total Opex		50	
2a	Regeneration cost of CHP	\$/T of product	30	Regeneration cost of CHP
2b	Opex (Utility cost for process including recycle of MeOH)	\$/T of product	20	Distillation and other utility cost
3.	Cash Cost (1 + 2)	\$/T of product	697	
4.	CAPEX (ISBL + OSBL)	MMS\$	150	Estimated for 250 KTPA production unit
5.	Capex Charge (25% return) (4*0.25/250 KTPA/1000)	\$/T of product	150	
6.	Life Cycle Cost (3 + 5)	\$/T of product	847	
7.	Market Price of VLSFO (<0.5% T'S')	\$/T	900	https://shipandbunker.com/prices/av/global/av-glb-global-average-bunker-price
8.	Product Margin (7 – 3)	\$/T	203	
9.	EBITDA (8 * 250 KTPA/1000)	MMS\$/y	51	
10.	Payback (4 / 9)	Year	3	

Table T7 shows the technoeconomic evaluation of ODS process using 5 wt.% V₂O₅/Al₂O₃ as catalyst, 30 (v/v) % CHP as oxidant and methanol as extractant. 250 KTPA commercial production is considered for IMO-2020 grade residual oil production plant in the calculation and assumed a CAPEX of 150 MMS\$, and CAPEX charge of 25% return. Price of refinery grade residual oil is typically available at 350 \$/T (avg.). Considering the 95% of solvent and 80% of oxidant recycle, cash cost per ton of IMO-2020 grade residual oil is about 697 \$/T. Price of VLSFO is fluctuating throughout the year, average price of 900 \$/T is considered for the calculation. Significant product margin of 203 \$/T of IMO grade residual oil with EBITDA 51 MMS\$/year and payback period of 3 years is obtained. This profit margin is lucrative for oxidative desulfurization of residual oil to produce IMO grade residual oil, however further fine tuning could be done considering miscellaneous factors.