

Supplementary

Heterostructure of vanadium pentoxide and mesoporous SBA-15 derived from natural halloysite for highly efficient photocatalytic oxidative desulphurisation

Manh B. Nguyen^{a,b}, Xuan Nui Pham^{c*}, Huan V. Doan^{c,d,*}

^a*Institute of Chemistry (IOC), Vietnam Academy of Science and Technology (VAST), 18 Hoang Quoc Viet, Cau Giay, Hanoi, Viet Nam*

^b*Hanoi University of Science and Technology (HUST), 01 Dai Co Viet Road, Hanoi, Viet Nam*

^c*Department of Chemical Engineering, Hanoi University of Mining and Geology, 18 Vien Street, Bac Tu Liem District, Hanoi, Viet Nam*

^d*School of Chemistry, University of Bristol, Bristol BS8 1TS, UK*

Corresponding authors' email addresses:

phamxuannui@gmail.com (XNP) and huan.doan@bristol.ac.uk (HVD)

Contents

1. Characterisation techniques	1
2. Additional information and results	2
2.1. Unit cell parameters of $V_2O_5/Fe-Al-SBA-15$ samples	2
2.2. XPS result of 40% $V_2O_5/Fe-Al-SBA-15$	3
2.3. EDX spectra of 40% $V_2O_5/Fe-Al-SBA-15$	3
2.4. Gas sorption results of $V_2O_5/Fe-Al-SBA-15$ samples	4
2.5. Bandgap energy calculation	5
2.6. Photodegradation of DBT over 40% $V_2O_5/Fe-Al-SBA-15$ catalyst	6
2.7. Kinetics of photocatalytic degradation	7

1. Characterisation techniques

The crystalline phase structure of the prepared materials was determined over the 2-theta range of 0.5–80 degrees (D8 ADVANCE, Bruker, Germany) using Cu K_α radiation ($\lambda = 0.154$ nm) as the X-ray source at a scan rate of 2° min^{-1} . FT-IR spectra were recorded on a Bruker TENSOR37 instrument. SEM images were made on a JSM 740, operating at an accelerating voltage of 200 kV. Energy-dispersive X-ray spectroscopy analysis (EDS) was measured on a JED-2300 with gold coating. The Brunauer–Emmett–Teller (BET) surface areas of the samples were evaluated by the N_2 adsorption isotherm at 77 K using a BET Sorptometer (Automated Sorptometer BET 201-A,

USA). The UV-Vis diffuse reflectance spectra (DRS) were measured with a Shimadzu UV2550 spectrophotometer. The PL spectra of the photocatalysts were detected using a spectrofluorometer Fluorolog FL3-22 JobinYvon-Spex, USA, using a 450W xenon lamp as an excitation source with an excitation wavelength of 400 nm. The surface electronic state was identified through X-ray photoelectron spectroscopy (XPS) performed on an AXISULTRA DLD Shimadzu Kratos spectrometer (Japan) using monochromatic Al K_{α} radiation (1486.6 eV). The Mott-Schottky measurement in dark condition was performed in the potential range from -0.5 to $+3$ V (V vs. Ag/AgCl). The intensity of sunlight on the surface of the reaction was measured by instrument LX1330B.

2. Additional information and results

2.1. Unit cell parameters of $V_2O_5/Fe-Al-SBA-15$ samples

Table S1. Unit cell parameters of $V_2O_5/Fe-Al-SBA-15$ samples

Samples	d_{100} (\AA°)	a_o (nm)
Fe-Al-SBA-15	90.63	10.46
10% $V_2O_5/Fe-Al-SBA-15$	93.64	10.81
20% $V_2O_5/Fe-Al-SBA-15$	96.03	11.09
30% $V_2O_5/Fe-Al-SBA-15$	101.28	11.69
40% $V_2O_5/Fe-Al-SBA-15$	103.54	11.96
50% $V_2O_5/Fe-Al-SBA-15$	101.15	11.68

- d_{100} , the space distance between (100) planes.
- a_o , lattice cell parameter of the hexagonal structure.
- Unit cell parameter determined from the position of the (100) diffraction line as $a_o = 2d_{100}/\sqrt{3}$

2.2. XPS result of 40%V₂O₅/Fe-Al-SBA-15

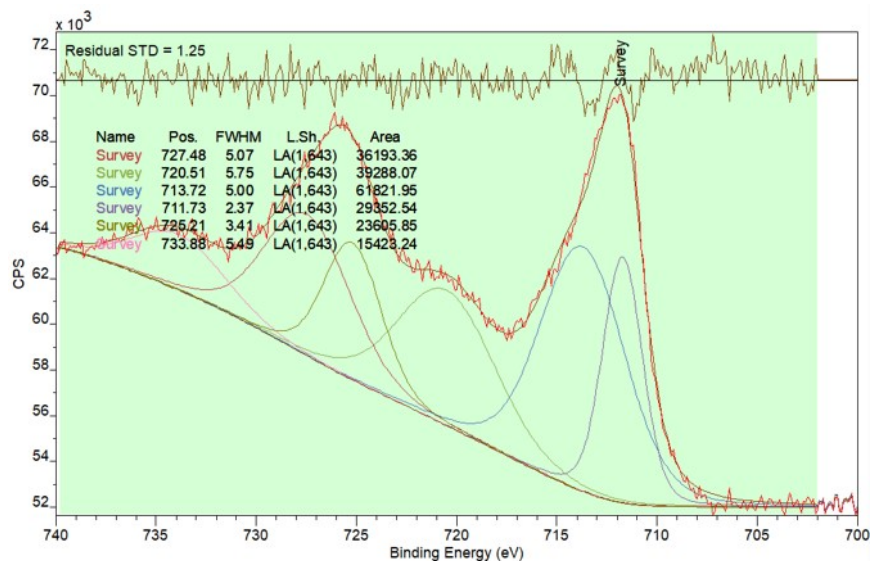


Fig. S1. The high-resolution XPS spectra of Fe 2p in 40%V₂O₅/Fe-Al-SBA-15

Table S2. Fe³⁺/Fe²⁺ ratio in 40%V₂O₅/Fe-Al-SBA-15

	Binding energy (eV)	Peak area	Total area	Fe ³⁺ /Fe ²⁺
Fe ²⁺	711.71	29352.54	52958.39	1.85
	725.21	23605.85		
Fe ³⁺	713.72	61821.96	98015.32	
	727.48	36193.36		

2.3. EDX spectra of 40%V₂O₅/Fe-Al-SBA-15

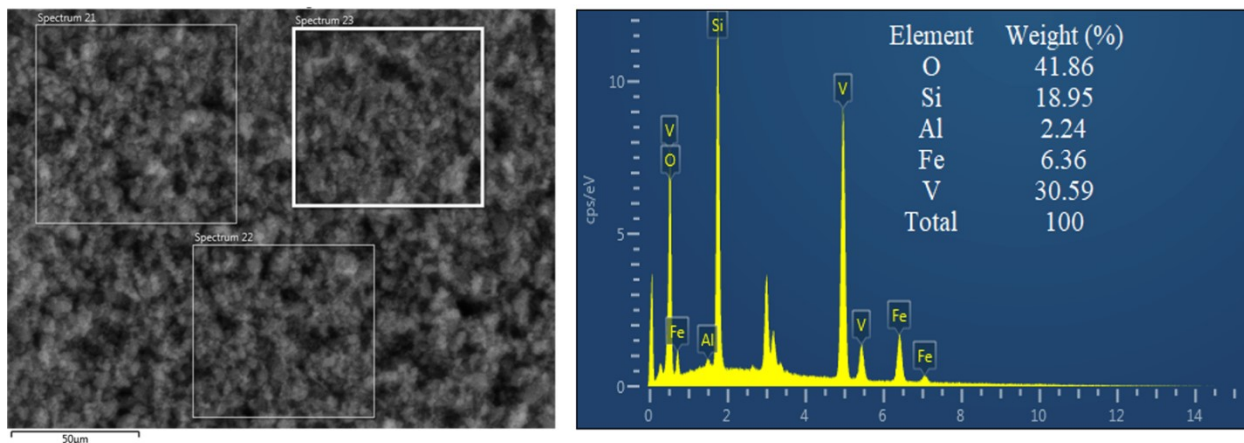


Fig. S2. EDX spectra of 40%V₂O₅/Fe-Al-SBA-15

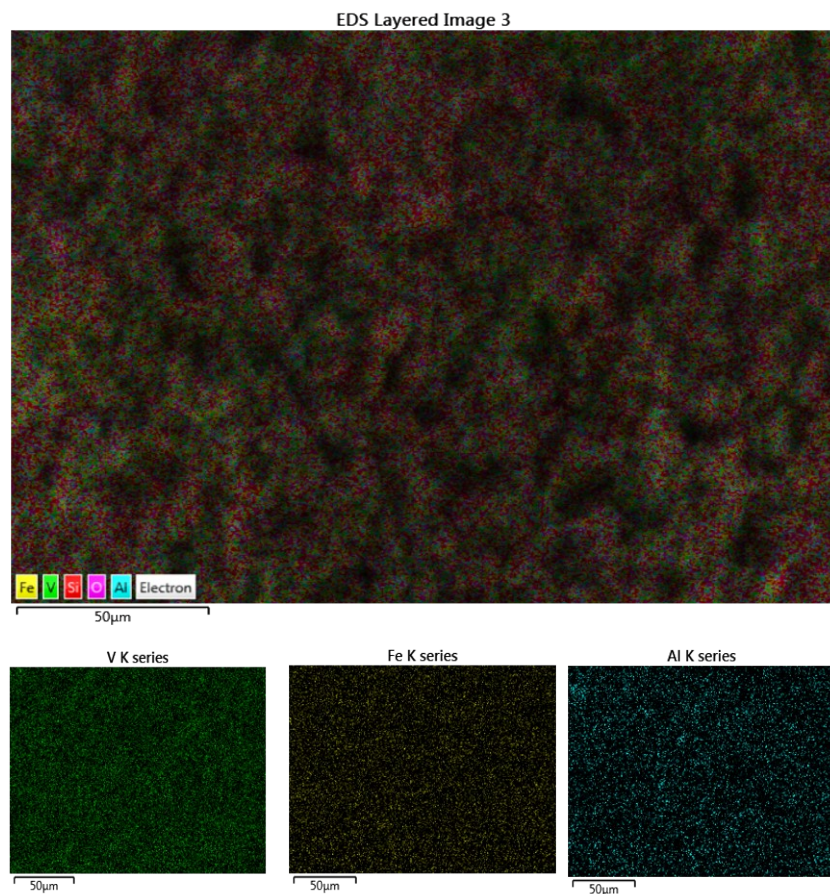


Fig. S3. EDX mapping images of 40% $V_2O_5/Fe-Al-SBA-15$ sample

2.4. Gas sorption results of $V_2O_5/Fe-Al-SBA-15$ samples

Table S3. Gas sorption results of $Fe-Al-SBA-15$ and $V_2O_5/Fe-Al-SBA-15$ samples

Samples	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	D (nm)
Fe-Al-SBA-15	824	1.46	8.13
10% $V_2O_5/Fe-Al-SBA-15$	740	1.34	8.15
20% $V_2O_5/Fe-Al-SBA-15$	666	1.18	8.13
30% $V_2O_5/Fe-Al-SBA-15$	593	1.09	8.07
40% $V_2O_5/Fe-Al-SBA-15$	550	0.86	7.96
50% $V_2O_5/Fe-Al-SBA-15$	418	0.59	6.18

- S_{BET} : Specific surface area calculated by the BET method.
- D_p : Pore diameter and V_p : Pore volume calculated from the N_2 desorption data based on the BJH method.

2.5. Bandgap energy calculation

The bandgap energy of the photocatalyst can be calculated using the following equation:

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (1)$$

where α can be determined according to the Kubelka-Munk theory; h is the Planck constant; ν is the frequency of light; A is absorption constant for direct transitions; E_g is the value of band gap energy; n depends on the characteristics of the transition in a semiconductor, for example, $n = 1, 4$ for direct and indirect transitions, respectively [1]. The energy of the bandgap E_g can be estimated from the x-axis interference of the tangent line of the graph $(\alpha h\nu)^2$ compared to the photon energy ($h\nu$). The bandgap energy E_g calculated from Equation 1 of Fe-Al-SBA-15, 10%V₂O₅/Fe-Al-SBA-15, 20%V₂O₅/Fe-Al-SBA-15, 30%V₂O₅/Fe-Al-SBA-15, 40% V₂O₅/Fe-Al-SBA-15 and 50%V₂O₅/Fe-Al-SBA-15 samples is approximately 2.26, 2.16, 2.0, 1.92, 1.88 and 1.96 eV, respectively. Bandgap energies of V₂O₅/Fe-Al-SBA-15 samples were 1.88–2.26 eV, which was lower than that of nano TiO₂ (3.2 eV). These results accord with their capacities for light absorption.

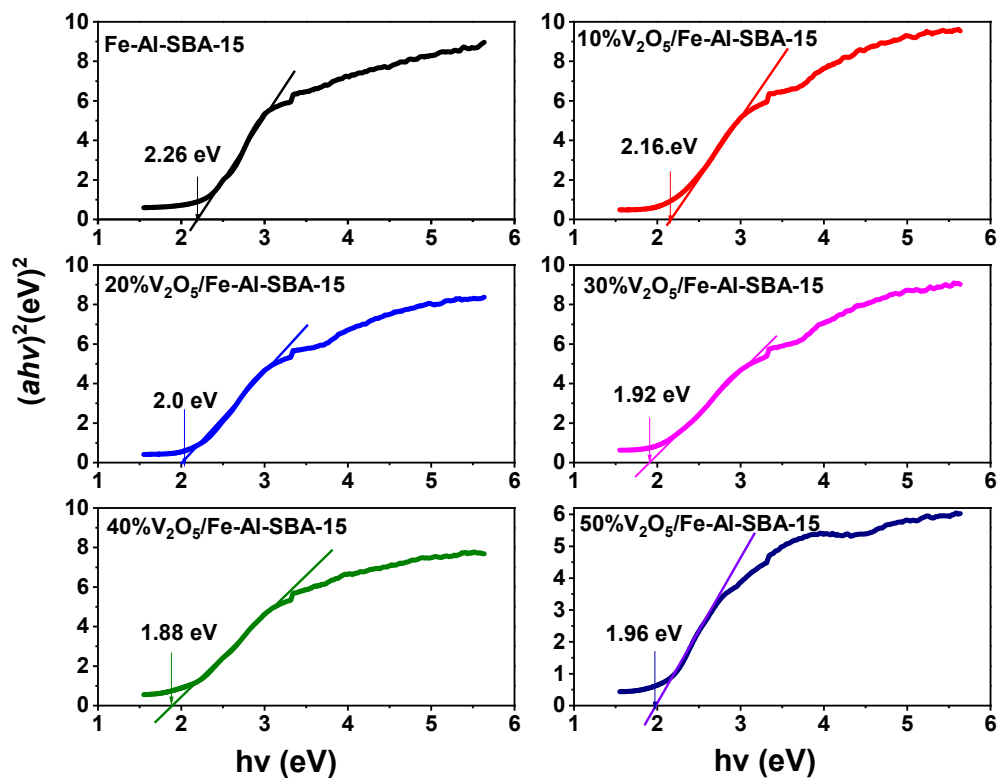


Fig. S4. Bandgap energies (E_g) of V₂O₅/Fe-SBA-15 samples

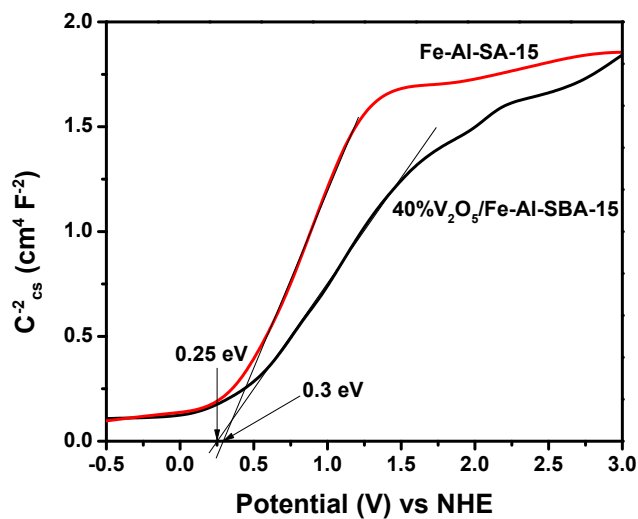


Fig. S5. Mott-Schottky plot for Fe-Al-SBA-15 and 40%V₂O₅/Fe-Al-SBA-15 samples. Mott-Schottky plots of Fe-Al-SBA-15 and 40%V₂O₅/Fe-Al-SBA-15 samples in 1M Na₂SO₄ solution at a frequency of 1 kHz in dark condition as a function of applied potential (V vs Ag/AgCl).

2.6. Photodegradation of DBT over 40%V₂O₅/Fe-Al-SBA-15 catalyst

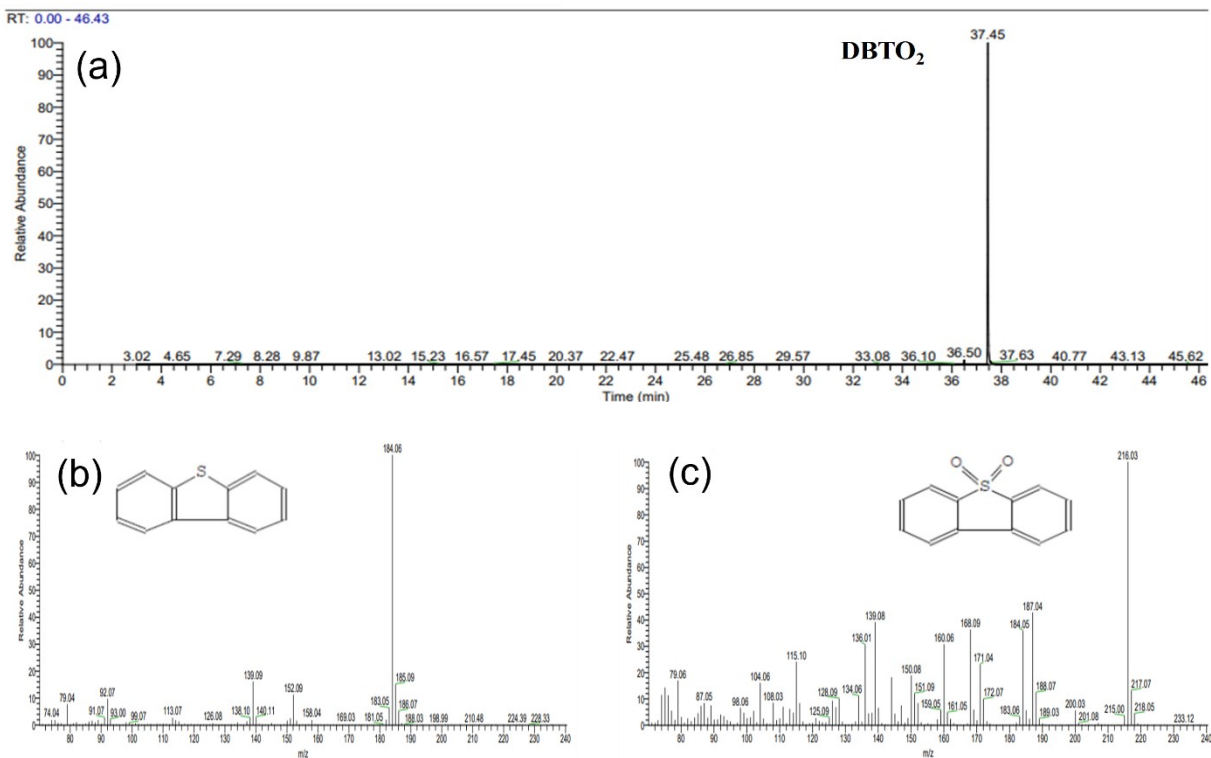


Fig. S6. (a) GC-MS spectra of the products in the photodegradation of DBT over 40%V₂O₅/Fe-Al-SBA-15 catalyst after 60 min (using 50 mg catalyst, 1 ml H₂O₂, 500 ppm DBT, at 70 °C). Further GC-MS analysis of the reaction product (b) compared to the initial reaction solution (c).

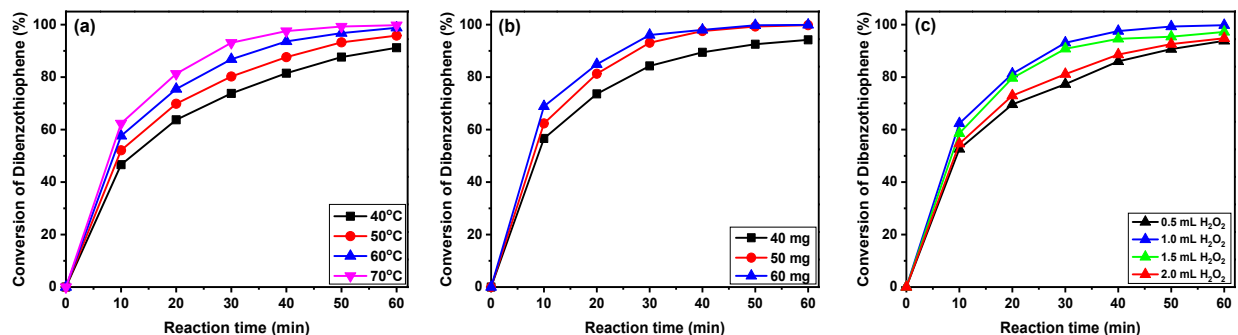


Fig. S7. Photodegradation of DBT over 40% $V_2O_5/Fe-Al-SBA-15$ catalyst at different conditions. (a) At temperatures ranging between 40 and 70 °C, $m_{catalyst} = 50$ mg, $V_{H_2O_2} = 1.0$ ml. (b) Using different amounts of catalyst (40 - 60 mg), $V_{H_2O_2} = 1.0$ mL, reaction temperature at 70 °C. (c) Using different amounts of H_2O_2 (0.5 - 2.0 ml), $m_{catalyst} = 50$ mg, reaction temperature = 70 °C

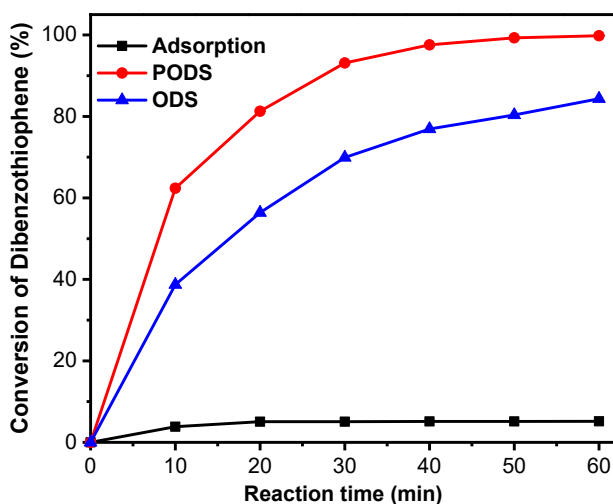


Fig. S8. The reaction of DBT (500 ppm) over 40% $V_2O_5/Fe-Al-SBA-15$ material (50 mg) at 70 °C under different conditions, i.e. adsorption without H_2O_2 in the dark, oxidative desulphurisation (ODS) with 1 ml H_2O_2 in the dark, and photocatalytic oxidative desulphurisation (PODS) with 1 ml H_2O_2 under natural sunlight

2.7. Kinetics of photocatalytic degradation

From the abovementioned experiments, all the optimal reaction conditions were used in the system, i.e., 1.0 ml of H_2O_2 , 50 ml of DBT (500 ppm DBT in *n*-octane), 50 mg of 40% $V_2O_5/Fe-Al-SBA-15$, and operating temperatures of 40 °C, 50 °C, 60 °C, and 70 °C. The photocatalytic degradation of DBT as a function of irradiation time in the presence of 40% $V_2O_5/Fe-Al-SBA-15$ could be described by the pseudo-first-order reaction, as shown in Equation 2:

$$-\ln\left(\frac{C_t}{C_0}\right) = k_p t \quad (2)$$

where C_t and C_0 are the concentrations at time t and time zero, respectively, k_p is the first-order reaction rate constant (h^{-1}), and t is the irradiation time (h). The data shown in Fig. S9 could be satisfactorily analysed by the first-order kinetic Equation 2 to obtain the rate constant.

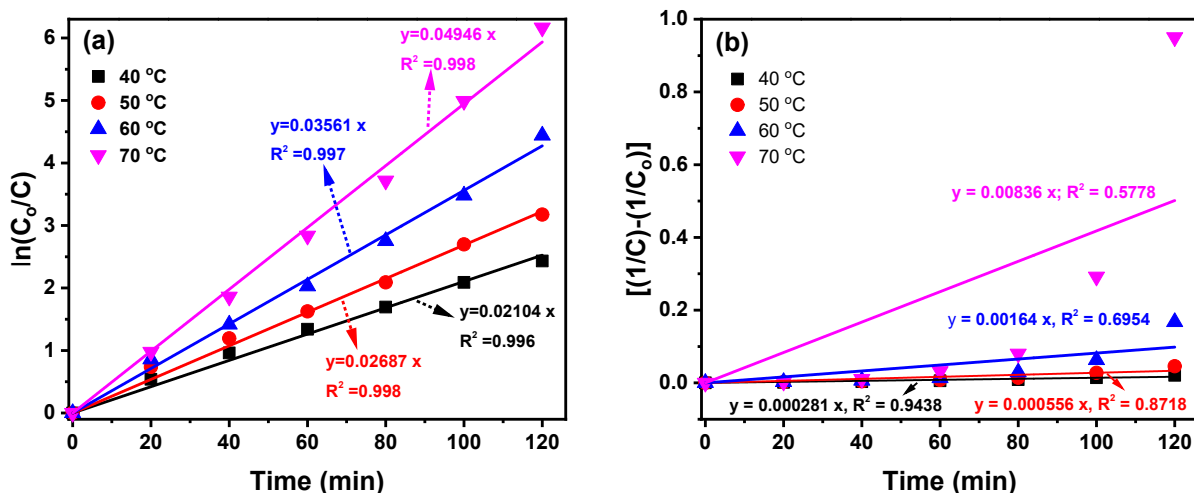


Fig. S9. Plots of (a) pseudo-first-order and (b) pseudo-second-order kinetic models for the degradation of DBT by photocatalytic oxidative desulphurisation at different temperatures

According to the plot shown in Fig. S9a, the first-order kinetic equation of the desulphurisation reaction of 40% $\text{V}_2\text{O}_5/\text{Fe-Al-SBA-15}$ was determined at different temperatures. That is, $y = 0.04209x$ with the value of correlation coefficient $R^2 = 0.996$, $y = 0.05374x$ with the value of correlation coefficient $R^2 = 0.998$, $y = 0.07123x$ with the value of correlation coefficient $R^2 = 0.997$, and $y = 0.09892x$ with the value of correlation coefficient $R^2 = 0.998$ at temperatures of 40 °C, 50 °C, 60 °C, and 70 °C, respectively.

All the linear graphs agreed with the first-order reaction ($R^2 > 0.99$). The kinetic rate constants (k_p) of 40 °C, 50 °C, 60 °C, and 70 °C were measured at 2.5254, 3.2244, 4.2738 and 5.9352 h^{-1} , respectively. The half-life of the experiment was calculated by substituting C_t with $C_0/2$. The results are shown in Equation 3:

$$t_{1/2} = \frac{0.693}{k_p} \quad (3)$$

where $t_{1/2}$ is the half-life (h).

According to the kinetics study, the half-life ($t_{1/2}$) of the DBT degradation reactions was determined to be 0.274, 0.215, 0.162, and 0.12 h at reaction temperatures of 40 °C, 50 °C, 60 °C, and 70 °C, respectively. These results indicate that as the relatively fast degradation rate of DBT

increased, the reaction temperature increased (70 °C), which was consistent with the increases in the reaction temperature and the reaction rate according to the Arrhenius Equation 5 [2] and resulted in a higher conversion of DBT.

Thus, the oxidative photocatalytic desulphurisation for DBT in the *n*-octane solvent using 40%V₂O₅/Fe-Al-SBA-15 was the pseudo-first-order reaction.

In contrast, if the reaction followed the second-order kinetics, the kinetic equation could be expressed as follows:

$$\frac{1}{[C]^{n-1}} = \frac{1}{[C_0]^{n-1}} + (n-1)kt \quad (4)$$

where C_t and C_0 are the concentrations at time t and time zero, respectively, k is the second-order reaction rate constant, t is the irradiation time (h), and n is the reaction order ($n = 2$ for the second-order equation). Plots were built to identify the relation between $[(1/C) - (1/C_0)]$ versus the irradiation time at different temperatures, as shown in Fig. S9b.

As calculated, the second-order reaction did not seem to be suitable for the sulphur removal reaction. The kinetic data collected at 70 °C yielded a considerably low correlation coefficient with the value of R^2 (0.57). In addition, the values obtained at 40 °C, 50 °C, and 60 °C did not converge, which showed an important fluctuation. These R^2 values were considerably lower in the pseudo-second-order reaction than in the pseudo-first-order kinetic reaction model ($R^2 > 0.99$), and the confidence value was insignificant for the former; hence, the pseudo-second-order reaction model was not considered for the photocatalytic degradation of DBT under sunlight irradiation.

The dependence of the rate constant k on the reaction temperature was expressed as an Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}} \quad (5)$$

Accordingly,

$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln A \quad (6)$$

where E_a is the apparent activation energy, A is the pre-exponential factor, R is the gas constant, and T is the reaction temperature (K). The Arrhenius plot considering the first-order reaction is shown in Fig. S9a. The apparent activation energy (E_a) was calculated from the slope and the intercepts of the Arrhenius plot with a value of 30.52 kJ mol⁻¹. This value was similar to the previously reported results; the activation energy was 32.5 kJ mol⁻¹ for DBT oxidation with C₅H₉NO.SnCl₂ coordinated ionic liquid [3]. Atsushi *et al.* reported that the E_a value for the oxidative desulphurisation of DBT was 32±2 kJ mol⁻¹ using MoO₃/Al₂O₃ catalyst [4]. Choi *et al.* reported that the E_a value for the oxidative desulphurisation of DBT was 29 kJ/mol using

polyoxometalate/H₂O₂ catalyst [5]. Huang *et al.* reported that the E_a value for the oxidative desulphurisation of DBT was 28.7 kJ mol⁻¹ using a catalyst of quaternary ammonium bromide and phosphotungstic acid [6]. Alwan *et al.* reported that the E_a value for the oxidative desulphurisation of DBT was 36.26 kJ mol⁻¹ using Fe₂O₃/GO catalyst [7].

References

- [1] M. Yang, W. Xu, J. Li, Z. Zhou, Y. Lu, *Optik (Stuttg)*. 193 (2019).
- [2] D. Xie, Q. He, Y. Su, T. Wang, R. Xu, B. Hu, *Cuihua Xuebao/Chinese J. Catal.* 36 (2015) 1205–1213.
- [3] F.T. Li, C.G. Kou, Z.M. Sun, Y.J. Hao, R.H. Liu, D.S. Zhao, *J. Hazard. Mater.* 205–206 (2012) 164–170.
- [4] A. Ishihara, D. Wang, F. Dumeignil, H. Amano, E.W. Qian, T. Kabe, *Appl. Catal. A Gen.* 279 (2005) 279–287.
- [5] A.E.S. Choi, S. Roces, N. Dugos, M.W. Wan, *Sustain. Environ. Res.* 26 (2016) 184–190.
- [6] G. Luo, Y. Lu, Y. Wang, D. Huang, 2007 AIChE Annu. Meet. (2007) 6221–6227.
- [7] H.H. Alwan, A.A. Ali, H.F. Makki, *Bull. Chem. React. Eng. Catal.* 15 (2020) 175–185.