Supplementary

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

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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\(_\alpha\) radiation (\(\lambda = 0.154 \text{ nm}\)) 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 Ka 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$_2$O$_5$/Fe-Al-SBA-15 samples

| Samples                  | d$_{100}$ (Å) | a$_o$ (nm) |
|--------------------------|---------------|------------|
| Fe-Al-SBA-15             | 90.63         | 10.46      |
| 10%V$_2$O$_5$/Fe-Al-SBA-15 | 93.64         | 10.81      |
| 20%V$_2$O$_5$/Fe-Al-SBA-15 | 96.03         | 11.09      |
| 30%V$_2$O$_5$/Fe-Al-SBA-15 | 101.28        | 11.69      |
| 40%V$_2$O$_5$/Fe-Al-SBA-15 | 103.54        | 11.96      |
| 50%V$_2$O$_5$/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%V$_2$O$_5$/Fe-Al-SBA-15

![XPS spectra](image1)

Fig. S1. The high-resolution XPS spectra of Fe 2p in 40%V$_2$O$_5$/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  |              |                     |

Table S2. Fe$^{3+}$/Fe$^{2+}$ ratio in 40%V$_2$O$_5$/Fe-Al-SBA-15

2.3. EDX spectra of 40%V$_2$O$_5$/Fe-Al-SBA-15

![EDX spectra](image2)

Fig. S2. EDX spectra of 40%V$_2$O$_5$/Fe-Al-SBA-15
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:

\[
ahv = A(h\nu - E_g)^{n/2}
\]

(1)

where \(\alpha\) can be determined according to the Kubelka-Munk theory; \(h\) is the Planck constant; \(\nu\) 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 \((ahv)^2\) compared to the photon energy \((hv)\). The bandgap energy \(E_g\) calculated from Equation 1 of Fe-Al-SBA-15, 10%V_2O_5/Fe-Al-SBA-15, 20%V_2O_5/Fe-Al-SBA-15, 30%V_2O_5/Fe-Al-SBA-15, 40% V_2O_5/Fe-Al-SBA-15 and 50%V_2O_5/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 V_2O_5/Fe-Al-SBA-15 samples were 1.88–2.26 eV, which was lower than that of nano TiO_2 (3.2 eV). These results accord with their capacities for light absorption.

![Fig. S4. Bandgap energies \((E_g)\) of V_2O_5/Fe-SBA-15 samples](image-url)
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%V₂O₅/Fe-Al-SBA-15 catalyst at different conditions. (a) At temperatures ranging between 40 and 70 °C, m\textsubscript{catalyst} = 50 mg, V\textsubscript{H₂O₂}=1.0 ml. (b) Using different amounts of catalyst (40 - 60 mg), V\textsubscript{H₂O₂}=1.0 mL, reaction temperature at 70 °C. (c) Using different amounts of H₂O₂ (0.5 - 2.0 ml), m\textsubscript{catalyst} = 50 mg, reaction temperature = 70 °C

Fig. S8. The reaction of DBT (500 ppm) over 40%V₂O₅/Fe-Al-SBA-15 material (50 mg) at 70 °C under different conditions, i.e. adsorption without H₂O₂ in the dark, oxidative desulphurisation (ODS) with 1 ml H₂O₂ in the dark, and photocatalytic oxidative desulphurisation (PODS) with 1 ml H₂O₂ 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 H₂O₂, 50 ml of DBT (500 ppm DBT in n-octane), 50 mg of 40%V₂O₅/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%V₂O₅/Fe-Al-SBA-15 could be described by the pseudo-first-order reaction, as shown in Equation 2:
\[-\ln\left(\frac{C_t}{C_o}\right) = k_p t\]  

(2)

where \(C_t\) and \(C_o\) 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.

According to the plot shown in Fig. S9a, the first-order kinetic equation of the desulphurisation reaction of 40%V\(_2\)O\(_5\)/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 \(C_o/2\). The results are shown in Equation 3:

\[
t_{1/2} = \frac{0.693}{k_p}
\]  

(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\%\(V_2O_5/Fe-Al-SBA-15\) was the pseudo-first-order reaction.

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

\[
\frac{1}{[C]^{n-1}} = \frac{1}{[C_o]^{n-1}} + (n-1)kt
\]

(4)

where \(C_t\) and \(C_o\) 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_t] - (1/C_o)\] 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:

\[
k = Ae^{\frac{E_a}{RT}}
\]

(5)

Accordingly,

\[
\ln k = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln A
\]

(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 \(C_5H_9NO\cdot SnCl_2\) coordinated ionic liquid \[3\]. Atsushi \textit{et al.} reported that the \(E_a\) value for the oxidative desulphurisation of DBT was 32±2 kJ mol\(^{-1}\) using \(MoO_3/Al_2O_3\) catalyst \[4\]. Choi \textit{et al.} reported that the \(E_a\) value for the oxidative desulphurisation of DBT was 29 kJ/mol using
polyoxometalate/H$_2$O$_2$ 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 Fe$_2$O$_3$/GO catalyst [7].

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