

Beneficial interaction of copper oxide and fibrous silica for enhanced photocatalytic desulphurization

C N C Hitam¹, A A Jalil^{1,2*}, N N S M Shobri¹, A A Fauzi¹

¹ School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, Malaysia.

² Centre of Hydrogen Energy, Institute of Future Energy, Universiti Teknologi Malaysia, Malaysia.

*aishahaj@utm.my

Abstract. Photocatalytic desulphurization (PDS) is considered as a promising technique to remove hazardous sulphur compounds from fuel oil due to its high catalytic activity, safety, low energy consumption, and low cost. In this work, fibrous silica KCC-1 was synthesized by hydrothermal method followed by incorporation of CuO by electrolysis. The catalyst was used for PDS of dibenzothiophene (DBT). The presence of bicontinuous concentric lamellar morphology with uniform spherical shape was confirmed by FESEM analysis. The phase and crystallinity of the catalysts was investigated by XRD, while the band gap energy was determined by UV-Vis DRS. The PDS performance of CuO/KCC-1 was compared with KCC-1, CuO/SiO₂ and SiO₂. It was observed that the photoactivity of CuO/KCC-1 was higher than other catalysts (62.6%), which is mainly due to its fibrous morphology and appropriate band gap energy, as well as synergistic role of both CuO and KCC-1. This fibrous type catalyst could be a promising candidate for environmental purification specifically in the sulphur removal.

1. Introduction

Desulphurization of fuels is crucial for reducing sulphur content in order to solve the worldwide environmental pollution issue [1]. During combustion of fuel, sulphur emits as sulphur dioxide (SO₂) or sulphate which is one of the main sources of air pollution and acid rain [2]. The conventional hydrodesulphurization (HDS) method suffers the harsh reaction condition, expensive catalysts, and high purity hydrogen requirement. In recent time, photocatalytic desulphurization has become the main interest among researchers due to its greener approach for conversion of organic contaminants into harmless compounds [3]. The DBT and its derivatives could be converted into the sulfoxide (DBTO) and sulfone (DBTO₂) using this method [4]. The widely used titanium dioxide (TiO₂) photocatalyst suffers several drawbacks including low specific surface area, poor charge carrier separation, and narrow utilization of solar light [5].

For those reason, various metal oxide photocatalysts with narrower band gap has been explored including AgO, CuO, Fe₂O₃, etc. Among them, CuO is considered as a promising candidate due to its appropriate band gap, economical, less toxicity, and abundant source [6]. Numerous studies has reported on the use of CuO for different photocatalytic applications such as decolourization of methyl orange (MO) [7], degradation of *p*- chloroaniline (PCA) [8], and removal of bisphenol A (BPA) [9].



However, this CuO require support materials for improved dispersion and surface area, as well as to prevent agglomeration.

In order to improve the dispersion of metal oxides for abundant active sites, several support materials has been utilized including mesostructured silica nanoparticles (MSN) [10], mesoporous titania nanoparticles (MTN) [11], carbon nanotubes (CNT) [12], etc. Fibrous silica (KCC-1) is considered as a new potential support candidate to design efficient photocatalysts for degradation of organic pollutants [13]. It was first discovered by Polshettiwar and co-workers, which then experiencing various modifications for enhanced performance in different applications [14-17]. Due to its several drawbacks, more modification is needed to improve its usage under visible light.

Herein we report the synthesis of KCC-1 and CuO supported on KCC-1 (CuO/KCC-1) via hydrothermal and electrochemical methods, respectively. The catalyst was used for visible-light photocatalytic removal of DBT. The physicochemical properties of the catalysts were well characterized by FESEM, XRD, and UV-Vis DRS. Thus, this present work is hoped to deliver initiative for future design approaches on photocatalytic removal of various organic contaminants as well as other application

2. Experimental

2.1 Materials

Cethyltrimethylammonium bromide (CTAB), urea, tetraethylorthosilicate (TEOS) and dibenzothiophene (DBT) were purchased from Merck. Toluene, butanol, acetonitrile and iso-octane were obtained from QRec. Meanwhile, tetraethylammonium perchlorate (TEAP) was synthesized by previous reported method [6].

2.2 Synthesis of catalyst

Fibrous silica KCC- 1 was fabricated by hydrothermal method as reported by previous study [15], while SiO₂ was obtained by calcining the commercial SiO₂. For KCC- 1, CTAB and urea were dissolved in distilled water and mixed with another solution consists of TEOS, toluene and butanol. Then, the mixture was vigorously stirred at 403 K, before cooled and centrifuged. After the precipitate was oven-dried for 12 h, the sample was calcined at 823 K for 6 h. Meanwhile, the 5 wt% CuO/KCC-1 and CuO/SiO₂ catalysts were synthesized by electrochemical method using KCC-1 and SiO₂ powders as support, respectively, according to earlier study [6]. An electrolysis cell was provided with a magnetic stirrer, a platinum plate (2 x 2 cm²) as cathode and a copper plate (2 x 2 cm²) as anode. Firstly, distilled water was used to dissolve TEAP supporting electrolyte, then KCC-1 or SiO₂ powder was added and stirred for 5 min. The electrosynthesis was conducted at 120 mA cm⁻² and 273 K under atmospheric pressure. After the required CuO weight was reduced, the sample was impregnated and oven-dried, and calcined at 550°C for 3 hours. For pure CuO, the electrolysis was conducted as above without addition of any support material.

2.3 Characterization of the catalyst

The morphological properties of the catalysts were examined using FESEM (JEOL JSM-6701F). X-ray diffraction (XRD) analysis on powder diffractometer (Bruker Advance D8, USA) were used to detect the phase and crystallinity of the catalysts. UV-Vis diffuse reflectance spectra acquired by a PIKE Technologies DiffusIR was employed to determine the absorbance spectrum of the catalysts for band gap measurement.

2.4. Photocatalytic desulphurization reaction

The photocatalytic desulphurization of DBT was conducted as described in the previous report [18]. 100 mg L⁻¹ of DBT in hexane was mixed with acetonitrile as extractant, followed by addition of 0.375 gL⁻¹ catalyst, and stirred in dark treatment for 30 min. After 30 min, the reaction solution was irradiated with visible light, and sampling for every 10 min until 2 hours. The sample was centrifuged

before being analyzed by UV-Vis spectrophotometer (Thermo Scientific Genesys10uv Scanning) to measure the initial and final DBT concentration. The desulphurization percentage was obtained using this equation:

$$D = (1 - C/C_0) \times 100\% \quad (1)$$

Where C_0 is the sulphur content of the initial solution at $t = 0$, and C is the sulphur content after last sampling.

3. Results and Discussion

3.1 Morphological studies

Figure 1 displays the FESEM images of KCC-1 and CuO/KCC-1. Figure 1A reveals the presence of uniform spherical shape with bicontinuous concentric lamellar structure of KCC-1, with particle size ranging from 200 to 400 nm. Meanwhile, Figure B shows the preservation of fibrous silica KCC-1 upon addition of CuO, which is consistent with previous reported study [15]. For CuO/SiO₂, the irregular shaped silica morphology is expected, a similar observation with those reported for Ni/SiO₂ in dry reforming of methane due to the similar synthesis procedure [16].

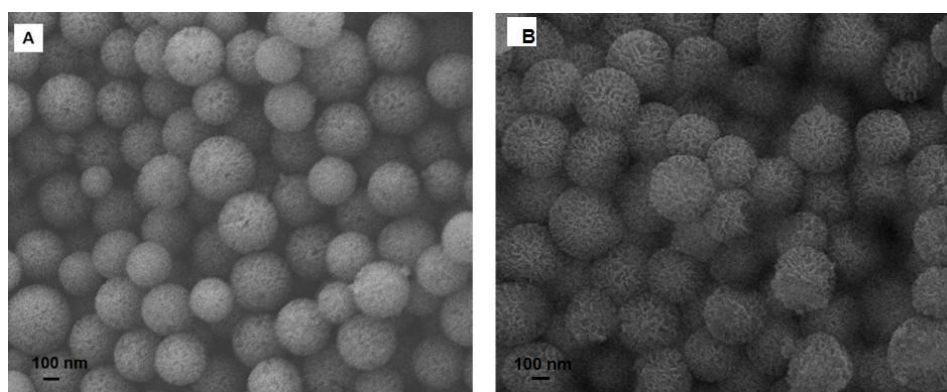


Figure 1. FESEM images of A) KCC-1 and B) CuO/KCC-1.

3.2 Structural properties

Figure 2 illustrates the XRD diffractogram of the bare and supported catalysts. The presence of amorphous structure in both KCC-1 and SiO₂ catalysts was signified by the existence of a broad peak between $2\theta = 20-30^\circ$ [19]. Figure 2 illustrates the XRD diffractogram of the bare and supported catalysts. The presence of amorphous structure in both KCC-1 and SiO₂ catalysts was signified by the existence of a broad peak between $2\theta = 20-30^\circ$ [19].

The inset figure shows the XRD pattern of the electrosynthesized CuO with diffraction peaks located at $2\theta = 32.5, 35.5, 38.7, 48.7, 53.4, 58.3, 61.5, 66.1$ and 68.1° , which were attributed to reflection lines of monoclinic CuO nanoparticles [20]. The decrease of the peak corresponding to amorphous silica of both KCC-1 and SiO₂ upon the introduction of CuO, suggesting partial blocking and distortion of the silica framework [21]. Besides, all distinct peaks of CuO were detected, which proving the successful loading of CuO dopant on both KCC-1 and SiO₂ catalysts, respectively.

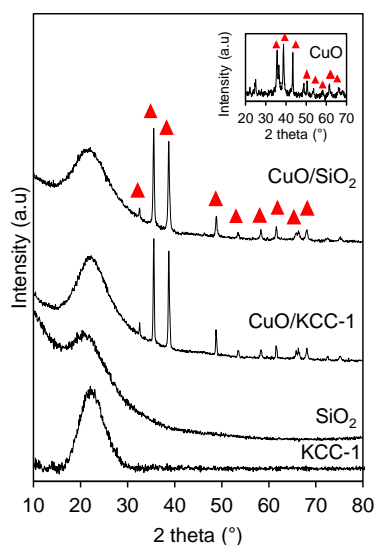


Figure 2. XRD pattern of the catalysts

3.3 Optical studies

Figure 3 displays the UV–vis DRS spectra of the catalysts. It was observed that KCC-1 had a significant absorption in the ultraviolet area at 320 nm and a red shift to a higher wavelength occurred after CuO was added.

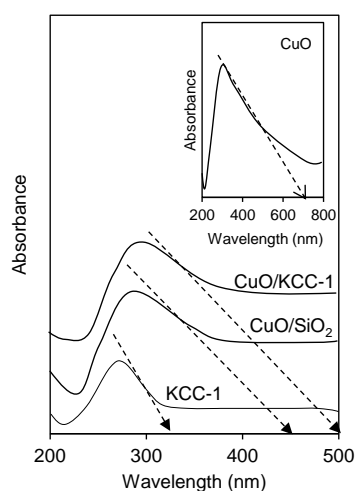


Figure 3. UV-Vis DRS spectra of the catalysts.

It was previously reported that the extension of the absorption spectrum is undoubtedly due to the interaction between the narrow band gap CuO (inset figure) and the support catalysts [22]. Based on this spectra, the band gap energies were calculated according to equation below;

$$E_g = \frac{1240}{\lambda} \quad (2)$$

The calculated band gap energy of the catalysts was tabulated in Table 1. The CuO/KCC-1 demonstrated a lower band gap energy than that of CuO/SiO₂, most probably due to the existence of more defect sites in KCC-1 as compared to SiO₂, as mentioned in earlier work [15]. It was also

previously revealed that the amount of surface defect had significantly affected the band gap energy of the catalysts [23].

Table 1. Band gap energy of the catalysts

Catalysts	Band Gap Energy (E_g)
KCC-1	3.88
CuO/SiO ₂	2.76
CuO/KCC-1	2.48
CuO	1.77

3.4 Photocatalytic desulphurization performance

Figure 4 displays the photocatalytic desulphurization performance of the catalysts under visible light irradiation. The CuO/KCC-1 demonstrated the highest photoactivity (62.6%) than that of CuO/SiO₂ (44.5%), KCC-1 (38.9%), CuO (31.4%) and SiO₂ (27%), mainly due to its fibrous morphology and narrowest band gap for the enhanced visible light absorption. Previous study has shown that the fibrous morphology contributed to the high surface area and high amount of surface defect [15]. These led to enhanced absorption of photon and adsorption of DBT molecules. Besides, it should be noted that the above mentioned criterion may also lead to an efficient charge carrier separation, which consequently resulted in an enhanced performance [24].

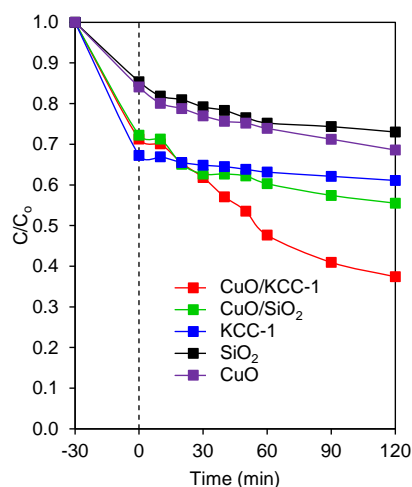


Figure 4. Photocatalytic desulphurization performance of the catalysts [0.375 g L⁻¹ catalyst, 100 mg L⁻¹ DBT, 120 min].

4.0 Conclusion

In this study, fibrous silica KCC-1 was fabricated via a hydrothermal method and loaded with CuO to form CuO/KCC-1 by electrochemical technique. The physicochemical properties of the catalysts were studied by FESEM, XRD and UV-Vis DRS analyses. The FESEM images reveals the existence of fibrous morphology KCC-1 in uniform spherical shape with bicontinuous concentric lamellar structure and particle size ranging from 200 to 400 nm. The XRD pattern shows that both KCC-1 and SiO₂ present as amorphous silica, and CuO was successfully loaded on both catalysts with the emerging of its characteristic peaks on the doped catalysts. Based on UV-Vis DRS, the absorption edge of KCC-1 shifted to higher wavelength by the addition of CuO, signifying a probable CuO/KCC-1 interaction and the role of CuO in altering the band energy of the catalysts. The photocatalytic desulphurization was conducted on 100 mgL⁻¹ of DBT and as expected, the highest performance was achieved using CuO/KCC-1 (62.6%). This is due to the presence of fibrous

morphology, incorporation of CuO, and the narrowest band gap. These criteria is synergistically crucial to achieve easier charge transfer and better charge carrier separation for enhanced photocatalytic performance.

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