Effect of doping Fe/Cu/Ti on WO₃ on furfural degradation

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Abstract. This research improved tungsten oxide catalysts to increase efficiency in photocatalytic degradation of furfural under visible light. The aim of this research was to compare the efficiency of modified tungsten oxide with undoped and commercial tungsten oxide. Tungsten oxide nanoparticles were doped with 3 single metals, which were Fe/Cu/Ti at 1%wt, 2%wt, and 3%wt, synthesized by flame spray pyrolysis technique (FSP) and then characterization by X-Ray Diffraction (XRD), N₂ adsorption/desorption (BET surface area analysis), UV-Vis Spectroscopy (UV-Vis). Photocatalytic degradation experiments using doped WO₃ were carried out with 5 ppm initial concentration of furfural solution using 0.6 M catalyst concentration under visible light. From the results, FSP-synthesized WO₃ has better efficiency in furfural degradation than the commercial WO₃. All catalysts have mesoporous structure because an average pore size is in the range of 6-10 nm. Among all synthesized and doped WO₃, it can be concluded that 3%wt Fe-doped tungsten oxide provides the highest acceleration rate in photocatalytic degradation of furfural.

1 Introduction

Tungsten oxide is one of the most promising inorganic materials which exhibit excellent electrochromic, photochromic and gasochromic properties and it has been widely investigated to be used in gas sensor application. However, tungsten oxide (WO₃) also has been developed to be a potential photocatalysts [1] because of its outstanding characteristics, highly stable physicochemical properties, good electron transport properties, nontoxicity and no-photo-corrosion. WO₃, with a band gap between 2.2 and 2.8 eV [2], is a visible light response catalyst, make it as an alternative choice for the photocatalytic oxidation of organic pollutants under solar irradiation instead of TiO₂. WO₃ can be synthesized by a variety of techniques such as precipitation [3], sol-gel[4], hydrothermal method[5], etc. However, the one of the disadvantages is that it has high possibility in occurrence of electrons-holes recombination. Thus, in order to increase the photocatalytic performance of WO₃, the addition of transition metals could either be alleviating of electrons-holes recombination process or supporting electrons to go to conduction band easier. Recently, there have been many studies and developments of tungsten oxide by doping of some transition metals, for example Fe and Mo [6-7] or making composite with other metal oxide such as TiO₂, CuO, AgIO₃ [8-12]. In this research, WO₃ samples were synthesized using flame spray pyrolysis, doped with Fe/Cu/Ti at different amount by wt%, characterized and tested the photocatalytic performance with 3 hours furfural degradation reaction under visible light.

2 Materials and method

2.1 Preparation of doped WO₃

Precursor solutions prepared with tungsten hexachloride used in WO₃ synthesis were fed into flame spray pyrolysis machine. Firstly, the precursor was prepared by dilution of tungsten hexachloride in ethanol and added 0.1M of Iron(III) nitrate nonahydrate, Copper(II) chloride and Titanium(IV) tetra isopropoxide with a calculation by wt% doping of single metal Fe/Cu or Ti equal to 1, 2, 3, respectively. The mixed precursor was injected through the center capillary of the flame spray pyrolysis nozzle with oxidizing gas into flame zone by syringe pump at flow rate was 5 ml/minute. Feed solution was dispersed with oxygen gas at flow rate of 5 l/min. Finally, after combustion, the precursor sprayed in FSP was then converted into WO₃ nanoparticles. WO₃ and doped WO₃ nanoparticles were collected on a glass fiber filter (Whatman GF/D, 15 cm diameter).

2.2 Characterization of WO₃ catalysts

X-ray diffraction was used to report phase composition of catalyst samples using CuK_α radiation with Ni filter in the 2 theta range of 10-80 degrees with a resolution of 2° per min. UV-VIS spectroscopy was used to measure the amount of light and intensity in the UV range and visible light (in the range of 190 nm to 900 nm) that absorbed by the sample to define bandgap energy of doped tungsten oxide samples by calculation through Kubelka-Munk equation. Brunauer-Emmett-Teller (BET) was used for analyzing the surface area of doped tungsten oxide samples by replacing the surface or porous surface with nitrogen gas. The pre-treatment using a helium gas flow of 50 ml / min at 180 °C for 3 hours was performed to remove the water contained in the catalyst and then tested by nitrogen gas substitution.

2.3 Photocatalytic activity measurement

The photoactivity measurements of prepared samples in furfural photodegradation were performed at an ambient

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temperature. The small scale-batch reactor is comprised of beaker within the black box with dimension length 30 cm, width 21.5 cm, and height 23 cm with 2 ventilation fan speed 1675 rpm inside. 4 compact 35 W Philips lamps with 2450 lumen/lamp (wavelength around 620 nm) were used as light source located about 10 cm far from beaker. In a typical process, aqueous suspensions of furfural 500 ml at 5 ppm initial concentration and 300 mg of nanocatalyst were placed in a vessel. Prior to irradiation, the suspension were magnetically stirred under dark for 30 min. 3 ml sample was drawn from furfural suspension every 10 min and removal of catalyst by centrifugation. The light absorption intensity at 273 nm was measured by UV-Vis spectrophotometer to identify furfural remaining concentration. The percentage of degradation was recorded as C/C_0 versus with time, while C is concentration of furfural for each irradiated time interval at wavelength 273 nm and C_0 is an initial concentration of furfural.

3 Results and discussion

3.1 X-Ray diffraction

In Figure 1, according to the JCPDS card no. 01-085-0950, all WO_3 catalysts were in monoclinic phase. Furthermore, there was also a peak corresponding to Cu at 2 theta equals to 41.85, 45.0, 47.42. After Fe/Cu/Ti metals were doped, the peak-height of metals slightly increased and the peak-height of tungsten somewhat decreased due to small level of doping. Doping metals would account for forming some oxide compositions of Fe/Cu/Ti and combining into the WO_3 crystalline structure. According to the 2 peaks of (002) and (200) WO_3 almost disappear to merely the rest of (020), it seems to be inferred that doping Fe possesses the most modified tungsten oxide phase, while the insignificant results appeared in case of Cu/Ti doping.

Figure 1 i), ii), iii) represent XRD patterns of Fe/Cu/Ti doped compared with undoped WO_3 (★, ▲, ●, ✧ represented WO_3 , Fe, Cu, Ti, respectively)

3.2 BET surface area and pore size distributions

From Table 1, BET surface area (S_{BET}) of synthesized WO_3 using flame spray pyrolysis has larger surface area than that of the commercial WO_3 . Flame spray pyrolysis method, FSP produces nanopowder of 20–100 nm average particle sizes (APS) with specific surface areas of 30–60 m^2/g whereas the commercial WO_3 is prepared by sol-gel technique [4]. When doping amount increased, the surface area was also increased. 1 wt% Cu-doped WO_3 has the largest specific surface area at 59 m^2/g . However after increasing Cu amount to 3 wt%, particles started to be agglomerate particles which lead to minimal surface area. From the results of an average pore size, it can be concluded that all catalysts have mesoporous structure.

Table 1 BET surface area and average pore size in nanometre of Fe/Cu/Ti-doped WO₃ compared to commercial and undoped WO₃

Catalyst samples	S _{BET} (m ² /g)	Average pore diameter (nm)
Commercial	8.26	6.69
Undoped-WO ₃	20.84	11.11
1%Fe-WO ₃	35.75	8.34
2%Fe-WO ₃	48.82	7.56
3%Fe-WO ₃	53.73	8.02
1%Cu-WO ₃	59.30	6.98
2%Cu-WO ₃	59.50	6.49
3%Cu-WO ₃	15.97	8.34
1%Ti-WO ₃	39.10	8.05
2%Ti-WO ₃	41.70	8.07
3%Ti-WO ₃	30.80	7.62

3.3 UV-Vis spectroscopy

After UV-Vis analysis, the ability in light absorbance of photocatalyst is also the significant characteristic that the promising photocatalyst should massive absorb and able to activate under visible wavelength [13-15]. The bandgap energy of all WO₃ samples was calculated by Kubelka-Munk relationship [16], shown in Table 2. In Kubelka-Munk relationship, equation (1), the graph is plot between transform reflectance spectra $(F(R_{\infty})h\nu)^{1/2}$ and $h\nu$.

$$F(R_{\infty}) = \frac{(1-R_{\infty})^2}{2R_{\infty}} \quad (1)$$

Transformation of absorbent unit into reflectance

$$A = \log I_0 (1/R) \quad (2)$$

$$R_{\infty} = 10^{-A} \quad (3)$$

Where A = absorbent unit
 h = Plank constant (6.624×10^{-34} Joules sec)
 ν = velocity of light (3.0×10^8 meter/sec)
 R_{∞} = reflectance unit

In Table 2, bandgap energy is the one of the key factors that directly impacts on the photocatalysis mechanism [17]. The narrower the bandgap energy, the lower the energy required on photocatalytic reaction. The commercial WO₃ has nearly equal bandgap energy and light adsorption under visible region when compared with an undoped WO₃. From this Table, it was obvious that 3%Fe-WO₃ has the smallest bandgap energy when compared with other catalysts. In case of Cu and Fe-doping, an increase in the doping amount leads to smaller the bandgap energy. Doping titanium enhances larger bandgap energy when compared with undoped and commercial WO₃ due to its wider bandgap energy, which would act as the pathway of electrons transition. However, there should be aware of doping amount as if too minimal bandgap energy might bring about electrons-holes recombination [19-20].

Table 2 Calculated bandgap energy of doped WO₃ compared with commercial and undoped WO₃

Catalyst samples	E _g (eV)
Commercial	2.68
Undoped-WO ₃	2.65
1%Fe-WO ₃	2.53
2%Fe-WO ₃	2.47
3%Fe-WO ₃	2.42
1%Cu-WO ₃	2.63
2%Cu-WO ₃	2.57
3%Cu-WO ₃	2.48
1%Ti-WO ₃	2.64
2%Ti-WO ₃	2.70
3%Ti-WO ₃	2.70

3.4 Photocatalytic activity

Photoactivity of synthesized and doped WO₃ was evaluated by furfural degradation under visible light for 3 hours. From the results, doping Fe/Cu/Ti on WO₃ shows difference influence on photocatalytic activity. Table 3 shows the total conversion of furfural using synthesized and various doped WO₃ after 3 hours. The percentage of furfural conversion (X) can be determined from the following equation [16];

$$X(\%) = \left(1 - \frac{C_A}{C_{A0}}\right) \times 100 \quad (4)$$

While C_A is equal to remaining concentration of furfural measured by UV-Vis, and C_{A0} is equal to an initial concentration of furfural. The photocatalytic degradation of furfural using WO₃ is the pseudo first-order linear reaction [21], the relationship between $-\ln(C_A/C_{A0})$ versus time is appeared to be linear, therefore the reaction rate constant (k value) can be calculated from equation (6), shown in Table 3.

Degradation reaction rate of furfural is assumed to be equal to R_A ,

$$R_A = -dC_A/dt \quad (5)$$

$$-\ln(C_A/C_{A0}) = kt \quad (6)$$

The catalyst that has lower C/C_0 shows the better the photocatalytic performance. From Table 3, it was found that FSP-synthesized WO₃ has better efficiency in furfural degradation than commercial WO₃ because FSP-synthesized WO₃ has larger surface area than commercial WO₃, resulted in more active sites. According to the equation (6), the highest k is belonged to 3 wt% Fe-doped WO₃, meaning that doping Fe at 3 % by weight is the most facilitated in furfural photocatalytic degradation. According to the results from Table 2, the bandgap energy of catalyst samples after doping with Fe or Cu were lower than that of undoped WO₃ because Fe and Cu assist in shifting to smaller bandgap energy. However, there is an optimum limit of Fe level since 2 wt% Fe-doped WO₃ and 3 wt%Fe-doped WO₃ obtain rather similar reaction rate, meaning nearly

equivalent in enhancing catalytic ability. In case of Ti, it was observed from the results that low amount of doping Ti onto WO₃ accelerates furfural degradation since the conversion of furfural from undoped WO₃ is lower than that from Ti-doped WO₃. However, the large amount of Ti doping showed detrimental influence on furfural photodegradation rate.

Table 3. The percentage of furfural conversion and reaction rate constant (k) after 3 hours photodegradation under visible light using different WO₃ samples.

Catalyst samples	Conversion(%)	k value (min ⁻¹)
Commercial	25±0.13	0.0015
Undoped-WO ₃	43±0.18	0.0027
1%Fe-WO ₃	36±0.2	0.0036
2%Fe-WO ₃	65±0.31	0.0083
3%Fe-WO ₃	68±0.28	0.0090
1%Cu-WO ₃	30±0.15	0.0021
2%Cu-WO ₃	32±0.24	0.0021
3%Cu-WO ₃	40±0.37	0.0028
1%Ti-WO ₃	67±0.4	0.0077
2%Ti-WO ₃	49±0.3	0.0044
3%Ti-WO ₃	38±0.08	0.0034

4. Conclusions

Tungsten oxide was successfully synthesized by Flame spray pyrolysis to use as a photocatalyst in furfural degradation. It was modified and developed photocatalytic activity by doping metal of Fe, Cu, and Ti at different mass fraction. From XRD, all the catalysts were appeared in the monoclinic phase. According to the light absorption results, it was found that after three metals-doping, the light absorption intensity increased and the bandgap energy changed. The effect on light absorption depends on type of metals. The addition of Fe helps in reducing the bandgap energy. The smallest bandgap energy is about 2.42 eV, as observed from 3 wt% Fe-doped WO₃. During photocatalytic degradation of furfural, among various catalysts, 3 wt% Fe-doped WO₃ shows the most potential in furfural degradation with the conversion of furfural equal to 68% and the highest reaction rate constant, k calculating based on the pseudo first order assumption.

Abbreviations

FSP: Flame Spray Pyrolysis
XRD: X-Ray Diffraction
UV-Vis: Ultraviolet Visible Spectroscopy
BET: Brunauer-Emmett-Teller
TEM: Transmission Electron Microscopy
EDS: Energy Dispersive X-Ray Spectroscopy
APS: Average Particles Size
X: The percentage of furfural conversion
C_A: The remaining concentration of furfural in aqueous solution
C_{A0}: The initial concentration of furfural in aqueous solution

S_{BET}: Surface area from BET analysis (m²/g)
E_g: bandgap energy (eV)
A.U.: Arbitrary Unit
cps: counts per second

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