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LETTER

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Preparation of iron doped carbon coated $W_{18}O_{49}$ and its Photoactivity.

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Iron doping to carbon coated $W_{18}O_{49}$ was carried out through solid-state reaction of $WO_{2.9}$ with iron acetate at 400 °C, followed by carbonization with poly(vinyl alcohol) (PVA) as carbon precursor at 800 °C in N_2 atmosphere. Photoactivities of these samples were confirmed by phenol photodecomposition in its aqueous solution. They revealed the photoactivity under visible light irradiation. Carbon coated $W_{18}O_{49}$ with iron exhibited higher photoactivity than it without iron. Addition of 1 % iron and 90/10 mixing ratio ($WO_{2.9}$ / PVA) derived the highest photoactivity to decompose the phenol.

Semiconducting photocatalysts have been recently used as a promising technology for the purification of water from organic pollutants in aqueous solution [1]. TiO_2 is one of the famous semiconductor photocatalysts [2]. It has been used to mineralize refractory organic pollutants in aqueous solution [3, 4]. However, large band gap (3.2 eV) having TiO_2 is corresponded to absorb only the ultra-violet (UV)-irradiation. Improvement of the efficiency of photoactivity becomes an important subject. Improvement of it has been carried out through anion doping, cation doping, coupling with other semiconductors, and preparation of reduced phases of TiO_2 shown at Ti_nO_{2n-1} [5 - 10]. It was also reported that several compounds which showed semiconductor property such as TaO_4 , $TaON$, and $BiNO_4$ revealed the activity under visible light [11 - 13]. Recently carbon coated $W_{18}O_{49}$ has been also reported as photocatalyst working under visible light [14 - 15]. $W_{18}O_{49}$ is a reduced phase of WO_3 and will be contained oxygen vacancies in crystal lattice. In present work, iron doping was attempted to improve the photoactivity for its $W_{18}O_{49}$.

Iron doping to the $WO_{2.9}$ was carried out through a solid-state reaction with iron (II) acetate. $WO_{2.9}$ and iron (II) acetate were mixed and then heat treated at 400 °C in N_2 to dope the iron. The proportion of different atomic ratios 0.5 %, 1 %, 5 %, and 10 % (Fe / W) were applied to evaluate the effect of amount of iron doping. Carbon coating to $WO_{2.9}$ with and without iron was carried out according to the coating of carbon to the ceramic powders [16]. $WO_{2.9}$ with and without iron was mixed with poly(vinyl alcohol) (PVA) in different mass ratios 90/10, 80/20, 70/30, 60/40 and 50/50 and then heat treated at 800 °C in N_2 to obtain the carbon coated $W_{18}O_{49}$. Heat treatment conditions were applied 5 °C /min and 60 ml/min in N_2 flow. Sample code was applied the following, x-FWPy, where x corresponds to amount of addition of the iron in percentage, F corresponds to the iron, W corresponds to the tungsten, P

corresponds to PVA and y corresponds to mixing ratio of PVA, respectively.

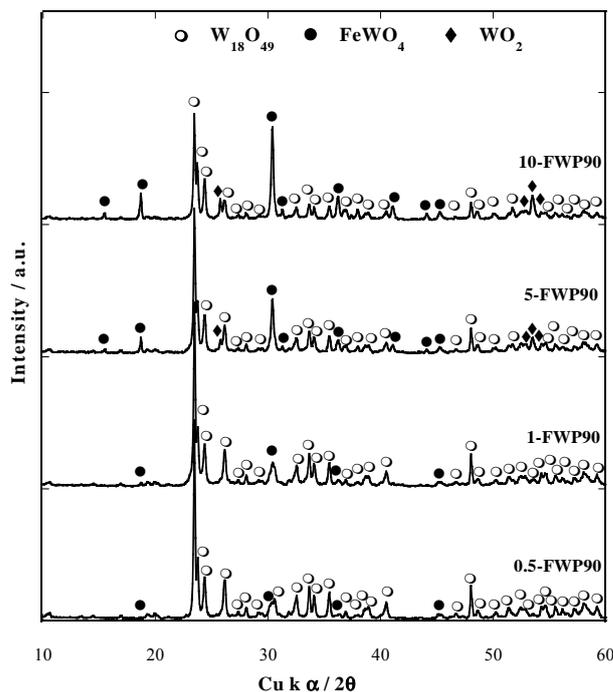


Figure (1) : XRD patterns of samples prepared.

After heat-treatment, the color of obtained samples changed from dark blue to brown with addition of iron. The amount of iron was determined by using atomic absorption spectrophotometer through extraction of 5 ml, 6 mol/dm³ HCl for 2 h. The photoactivities of samples were evaluated

through the photodecomposition of phenol in its aqueous solution of concentration 5.3×10^{-4} mol/dm³ in initial. Carbon coated samples dispersed in phenol solutions were held in the dark to saturate the phenol onto the carbon thin layer deposited on W₁₈O₄₉ surface. After saturation of it, visible light (the strength of 261 μW/cm² in the wavelength range from 400- 700 nm) was irradiated by using fluorescent lamp. The residue concentration of phenol was determined by using high performance liquid chromatography (HPLC) with ultra-violet (UV) detector on an ODS-100S column using 50 % MeOH / 50 % water as mobile phase at 1 ml/min of flow rate. The concentration of phenol was measured at the wavelength (λ) of 269 nm.

Figure (1) indicates the changes in the crystal phase with addition of the iron. Reduced phase W₁₈O₄₉ has recognized on XRD pattern. Its deposition decreased with increasing amount of addition of the iron. On the other hand, the increase of amount of iron derived the deposition of FeWO₄. Small amount of WO₂ phase was observed in addition of 5 and 10 % iron. These results revealed that the reduction process through carbonization proceeded to the deposition of WO₂. The absorbances of samples were measured in the wavelength range 250 - 700 nm by using diffuse reflectance spectrophotometer. The carbon coated W₁₈O₄₉ with iron showed the absorbance in the whole wavelength similar to carbon coated W₁₈O₄₉ [15]. Their absorbance decreased with increasing amount of addition of iron as shown on figure (2). It could be related to the change in sample color due to the amount of iron added.

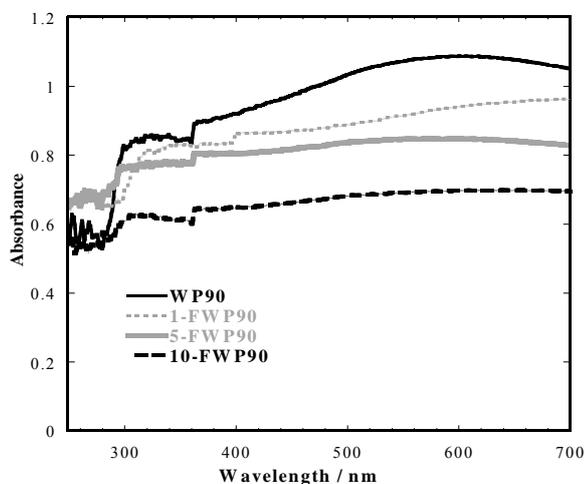


Figure (2) : UV – VIS absorption spectra of samples prepared.

It is reported that the thin carbon layer on the photocatalyst particle by carbon coating is formed [17]. It seemed to carry out the formation of thinner carbon layer in this case, because PVA precursor is consumed in the reduction of WO_{2.9}. This carbon thin layer will be working as an adsorption layer of the pollutant [15]. The iron content which included actually 0.32, 0.72, 1.03 and 0.862 (wt %) was confirmed by atomic absorption spectrophotometer and it corresponded to addition of amount of iron 0.5 %, 1 %, 5 % and 10 %, respectively. The content of iron was saturated around 5 % amount of addition of the iron. This saturation is related the deposition of FeWO₄. Iron doping to carbon

coated W₁₈O₄₉ seems to be a little. Amount of its doping is strongly regarded as being concerned in the formation of the solid solution between iron and W₁₈O₄₉.

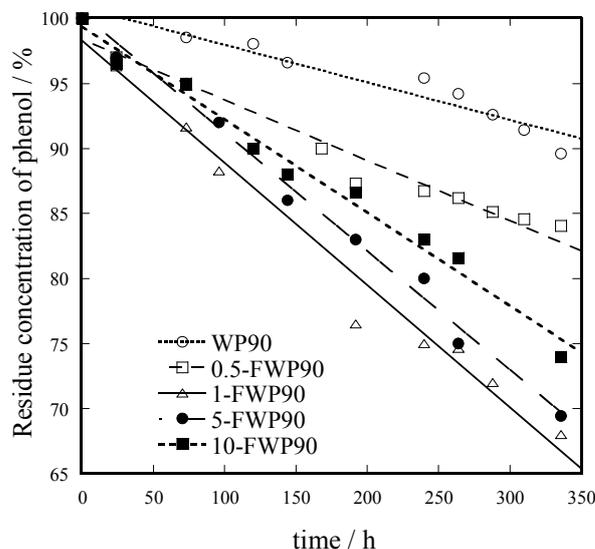


Figure (3) : Changes in residue concentration of phenol under visible light irradiation for carbon coated W₁₈O₄₉ with and without iron doping.

Figure (3) shows the changes in residue concentration of phenol under visible light irradiation for carbon coated W₁₈O₄₉ with and without addition of iron. Iron doping for carbon coated W₁₈O₄₉ showed higher photoactivity for phenol decomposition in comparison with iron undoped samples. The highest photoactivity of phenol decomposition had observed on 1 % addition of iron. The decreasing of photoactivity through increasing with addition of the iron related to the deposition of FeWO₄ and derived decreasing in the deposition of W₁₈O₄₉ phase with the addition of iron.

The effect of amount of carbon on the photoactivity of W₁₈O₄₉ was also examined. Figure (4) shows the changes in residue concentration of phenol under visible light irradiation for carbon coated W₁₈O₄₉ prepared with 1 % addition of the iron and with different mixing mass ratios of PVA. Its results revealed that mixing ratio 90/10 derived the highest photoactivity under visible light. Carbon layer covered on W₁₈O₄₉ surface might be worked for adsorption of phenol and concentration of it. It also might be accelerated the photodecomposition of phenol on W₁₈O₄₉ particles. The photoactivity might be depending on the diffusion of pollutants into the porous carbon layer to reach the active centers on the photocatalyst particles [17]. Thickness of carbon layer and amount of pollutant in its layer which is optimum for the diffusion in its layer is seemed to be existed.

It is considered that the iron doping of less than 1 % such as 0.72 % and 90/10 mixing ratio of PVA are effective in the improvement on the photoactivity. Preparation and its improvement of the photocatalyst which worked in the visible light succeeded by the addition of iron and coating of carbon layer.

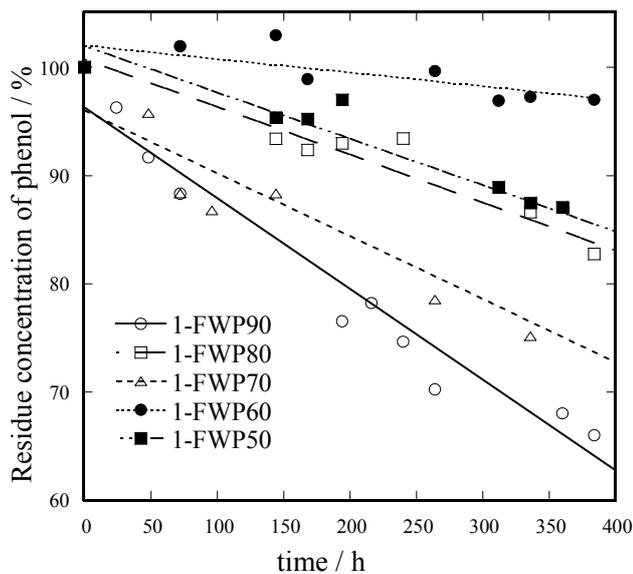


Figure (4) : Changes in residue concentration of phenol under visible light irradiation.

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