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Hydrothermal Synthesis and Catalytic Activity of a Nanosized $Fe_2V_4O_{13}$ Material in Heterogeneous Fenton-like Reaction for Degradation of Organic Compounds

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ABSTRACT

In this research, the nanosized $Fe_2V_4O_{13}$ complex oxide material was synthesized by the hydrothermal method. Its structure, morphology characterization, and other properties were determined using X-ray, SEM, EDX, and DTA-TG methods. The catalytic activity of the material was evaluated in terms of the decolorization and the degradation of the Indigo carmine dye. The optimal condition for the degradation and the reusability of the catalyst were determined. The results showed that the heterogeneous Fenton-like catalyst is a promise for wastewater treatment.

Introduction

The Fenton system (Fe^{2+}/H_2O_2) was first invented in 1894 by H.J. Fenton. Since then, it has become a very common oxidation system for the degradation of persistent organic pollutants in aqueous environments [1]. The degradation process is driven by the generation of hydroxyl radicals ($OH^\bullet$), one of the strongest oxidants which can react non-selectively with various types of organic compounds [2]. However, this process suffers from limitations due to the precipitation of iron ions at pH greater than 3 and the difficulty of separating the catalytic species from the product. In recent decades there has been renewed interest in Fenton-like systems, particularly hetero-Fenton oxidation based on iron oxides or zerovalent iron, which are used as catalysts instead of the ferrous ions [3]. The advantages of such catalysts are their reusability and higher pH range [4] compared to the conventional Fenton reagent.

The effectiveness of the catalysts can also be enhanced thanks to the combination of iron oxide with other elements such as Mn, Co, and V,... [5]. Among them, $Fe_2V_4O_{13}$ presented a potential candidate for the Fenton-like oxidation [6, 7].

This paper aims to study the synthesis and characterization of $Fe_2V_4O_{13}$ using hydrothermal methods. The effects of synthetic parameters such as reaction temperature, reaction time, and annealing temperature on the catalytic activity of the catalysts were investigated. The catalytic activity was evaluated using indigo carmine (Ind) as a model organic compound. An oil-polluted water sample was used to assess the effectiveness of the catalyst in the Fenton oxidation process for the treatment of real industrial wastewater.

Experimental

Ammonium metavanadate (NH_4VO_3, 99,9 % w/w), ferric nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$, 99,9 % w/w), nitric acid (HNO_3, 70 % w/w), and ammonia solution (NH_3, 25% w/w) were purchased from Aladdin, China). Hydrogen peroxide solution (H_2O_2, 30 % w/w) and indigo carmine were from Merck. Zeolite 4A was obtained from China. Other chemicals were from

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Analar, England. All chemicals were at analytical grade and used as received.

The $Fe_2V_4O_{13}$ oxide was prepared using a hydrothermal method. Firstly, 50 mL of 0.025 M $Fe(NO_3)_3$, 50 mL of 0.05 M NH_4VO_3, and 10 mL of 1 M HNO_3 were sequentially added into a 250 mL three-necked flat-bottom flask. The reaction mixture was heated to 80 °C under vigorous stirring. Next, pH of the solution was adjusted to 10 using a 25 % NH_3 solution, and the reaction mixture was transferred into a 100 mL Teflon autoclave for hydrothermal treatment. The reaction temperature was kept constantly at 80 °C for 10 hours, then naturally cooled to room temperature. The resulting precipitate was separated by means of centrifugation at a rate of 4000 rpm and washed with double distilled water several times. Finally, the precipitate was dried at 100 °C for one hour and annealed at 500 °C for 5 hours, with a heating rate of 10 °C per minute. For studying the optimal conditions of the material synthesis, an experiment series were carried out. All other parameters were kept the same as described above. The differences were the reaction temperature (60 °C, 80 °C, or 100 °C) or the reaction time (5, 10, 15h), or the annealing temperature (not being annealed, 200 °C, 500 °C, or 600 °C). The materials were coded as X.Y.Z (X: crystallization temperature in Celsius, Y: crystallization time in minutes, and Z: annealing temperature in Celsius). Characterization of $Fe_2V_4O_{13}$ was performed using XRD (40kV, 40 mA, CuKα, D8 Advance, Burker, Germany), SEM (using JEOL JSM – 7600F, America, coupled with an energy dispersion X ray detector (EDS), DTA – TG (TGA209F1, NETZSCH, Germany; temperature range of 20 °C – 800 °C, a heating rate of 0,001 to 200K/min.), and UV–Vis spectrometer (DR6000, Hach, Germany)

The efficiency of catalytic activity was evaluated via the color removal of Ind by measuring the absorbance of Ind (at the wavelength of 612 nm) at time intervals.

The treatment of the oil-and-grease polluted wastewater (taken from a motorbike garage in Hoang Mai Road, Hanoi) was conducted with 100 mL of a mixture consisting of 50 mL origin sample, 0.3 $g.L^{-1}$ $Fe_2V_4O_{13}$, 1.10^{-4} M $HClO_4$, and 10 mM H_2O_2 at 30 °C After 2 hours, the mixture reaction was stopped by removing the catalyst. The unreacted hydrogen peroxide was removed using Na_2SO_3. An International Standard Method (ISO 6060:1989 standard) was used to determine the COD of reaction solutions.

Results and discussion

Characterization of the obtained catalyst materials

Figure. 1. shows the XRD pattern of the material prepared at 80 °C in 10 hours and annealed at 500 °C in 5 hours. The feature peaks of iron tetrapolyvanadate ($Fe_2V_4O_{13}$) can be observed at 12.5°; 18.8°, 22.6°, and 26.6° that are assigned to the monoclinic phase. This XRD pattern is very similar to the JCPDS card No 39-08930 [8]. The crystalline phase ratio of the material was about 86.31 %.

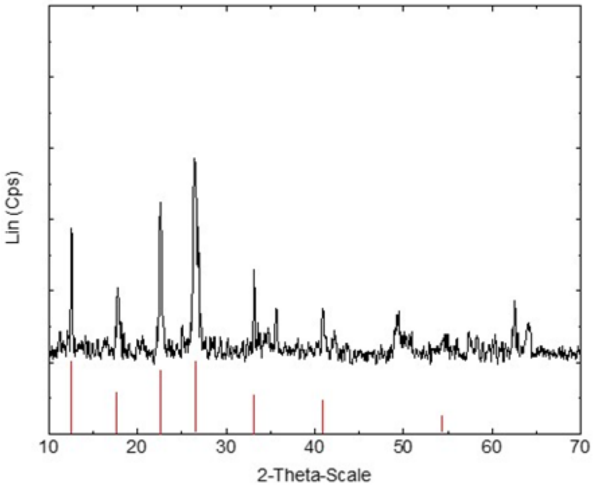


Figure 1: X-ray pattern diagram of $Fe_2V_4O_{13}$, synthesized at 80 °C in 10 h and annealed at 500 °C. The red bar indicates the standard JCPDS 39-08930

The Fe/V ratio is close to 1:2 which was found by EDX analysis (Figure. 2), confirming the $Fe_2V_4O_{13}$ species.

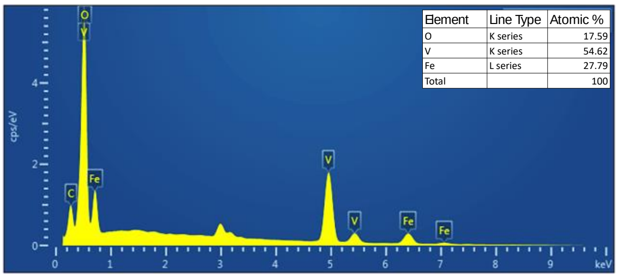


Figure 2: EDX spectrum of $Fe_2V_4O_{13}$, synthesized at 80 °C in 10 h and annealed at 500 °C. The inset is the atomic ratio of the elements

To study the thermal stability of the complex oxide $Fe_2V_4O_{13}$, thermal analyses were performed. The obtained results are depicted in Figure. 3. The thermogravimetric trace (TG) shows two mass-loss stages of 10.59 % and 3.69 %, respectively. This implies the dehydration and ammonium/nitrate compounds decomposition processes, corresponding to the temperature ranges from 25 °C to 250 °C and from 250 °C to 450 °C. The peak at 104.4 °C in the DTG curve shows the point where the mass reduction happened fastest, relating to the vaporization of non-bounded water. In the DTA curve, a peak at 560 °C indicates an exothermic effect of the solid. It can be assigned to a structurally changing process from an amorphous phase to a crystalline one. This observation is similar to the previous works [7].

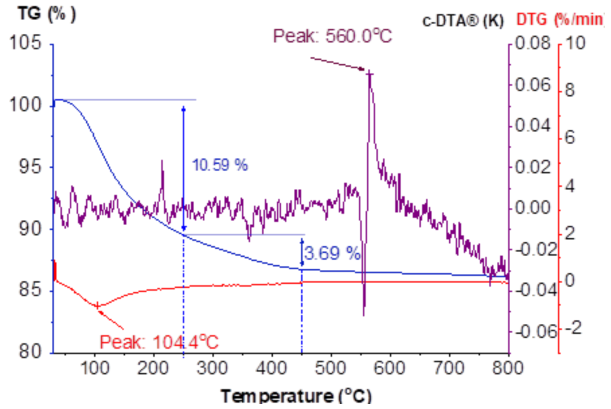


Figure 3: TG, DTA, and DTG (heating rate 10°C min^{-1}) curves of $Fe_2V_4O_{13}$

SEM image of the material shows the dumbbell-shaped morphology of the particles with an average size of 20 × 50 nm (Figure. 4).

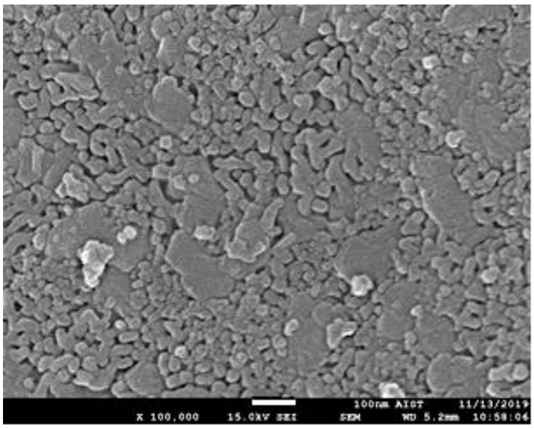
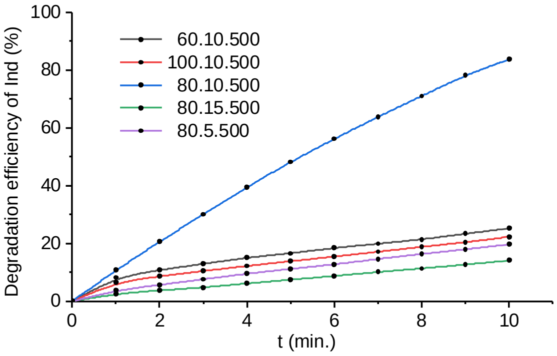


Figure 4: SEM image of $Fe_2V_4O_{13}$ materials

The characterization indicates the nano size of obtained $Fe_2V_4O_{13}$. The preparation parameters can impact the catalytic activity of this material.

The catalytic activity of $Fe_2V_4O_{13}$ in degradation of indigocarmine

To investigate the catalytic activity of $Fe_2V_4O_{13}$, indigo carmine was used as a model organic compound in the decomposition reaction using hydrogen peroxide catalyzed by the complex oxide. The catalyst synthesis conditions were optimized, including reaction temperature, reaction time, and annealing temperature. Figure. 5 exhibits the effect of reaction temperature and reaction time on the catalytic on the color removal of indigo carmine. The results show that the sample that performed the highest degradation efficiency was synthesized at the condition: reaction temperature of 80 °C, reaction time of 10 hours, and annealing temperature of 500 °C. The degradation efficiency of indigo camine reached 90 % within only 10 minutes.



m ($Fe_2V_4O_{13}$) = 2 mg; $[H_2O_2]_o$ = 0.3 mM ; $[Ind]_o$ = 0.1 mM;
pH = 4; T = 298 K

Figure 5: The effect of synthetic parameters of $Fe_2V_4O_{13}$ on the Indigo carmine degradation efficiency: reaction temperature of 60, 80, and 100 °C; reaction time of 5, 10, and 15 h; annealing temperature of 500 °C

The reaction rate constants were calculated using a pseudo-first-order reaction model from the kinetic curves in Figure. 5. The results were collated in Table 1.

Table 1: The reaction rate constants and corresponding correlation coefficients

Sample	k (min^{-1})	R^2
60.10.500	0.0319	0.9733
100.10.500	0.0270	0.9820
80.10.500	0.1580	0.9849
80.15.500	0.0153	0.9977
80.5.500	0.0226	0.9962

Reaction temperature plays an important role in the nucleation stage. The highest rate constant is achieved at 80 °C. The temperature of 60 °C is predicted to be insufficient to create a premise for nucleation from which precipitation of metal hydroxide molecules in the hydrothermal vessel takes place. However, at 100 °C, the reaction solution consisting of metal salts is rapidly hydrolyzed so that co-precipitation does not occur in both metals when the pH is raised to 10 with NH_3. The resulting precipitate is predicted to consist of distinct metal oxides with low catalytic activity [9].

As for the precipitation time factor, when increasing the reaction time from 5 hours to 10 hours, the indigo carmine treatment efficiency increased markedly from 20 % to more than 90 % (Figure. 5). The increased precipitation time allows the complex oxide to have enough time for the nucleation and precipitation processes to determine the grain size as well as the crystal structure. However, the treatment efficiency decreased significantly when the precipitation time increased from 10 hours to 15 hours. The phenomenon can be explained as follows: complex oxide particles clump when the reaction time is exceeded, causing the grain size to increase. It results in the decrease of active sites, thereby reducing the catalytic activity.

In addition, the temperature of thermal treatment for $Fe_2V_4O_{13}$ is also an essential factor (Figure. 6).

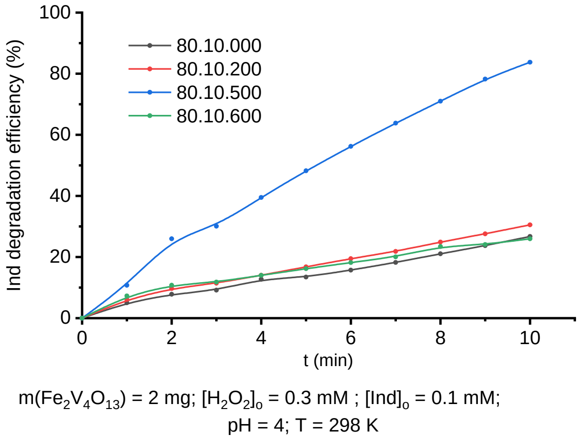


Figure. 6: The efficiency of Ind oxidation using H_2O_2 catalyzed by $Fe_2V_4O_{13}$ with different synthesis conditions: reaction temperature of 80 °C; reaction time of 10 h; no annealing or annealing temperature of 200; 500 and 600 °C

Figure. 6 indicates that the material has the highest catalytic activity at the annealing temperature of 500 °C. The degree of indigo carmine degradation reached about 90 % after 10 min. At the conditions of calcination temperature of 200 °C, 600 °C, or no anneal, the catalyst material only gives about 20 % indigo carmine decomposition after 10 minutes.

The result shows that the crystallization process only starts to occur at a specific temperature. At temperatures lower than 500 °C, the crystallization process does not occur, leaving the crystalline structure of the material in an amorphous state, creating very few active sites. In contrast, at 600 °C, the material is predicted to have a melting process that causes the forming lattice to be broken. Both of the above processes cause the catalytic activity of the material to be significantly reduced due to the lack of active centers where the electron exchange reaction takes place to create the active radical HO•.

The catalytic stability of $Fe_2V_4O_{13}$

During actual application, the long-term stability of a catalyst is crucial. In order to evaluate the repeatable use of the catalyst, $Fe_2V_4O_{13}$ was immobilized on zeolite 4A using hydrothermal treatment. The control experiment reveals that zeolite itself does not affect the degradation of indigo carmine dye.

The obtained results of catalytic testing for $Fe_2V_4O_{13}$ are depicted in Figure. 7. It can be observed that after the first run, the heterogeneous Fenton-like catalyst almost remained its catalytic activity about 80% in the subsequent three runs. After the first run, the reduction in catalytic activity could be due to a weak combination of the catalytic material and the support matrix. Therefore, some parts of the catalyst might leak into the reaction medium. Another possible reason is the aging of $Fe_2V_4O_{13}$ to a more stable state. However, the following three runs indicated the reasonable stability of the catalyst.

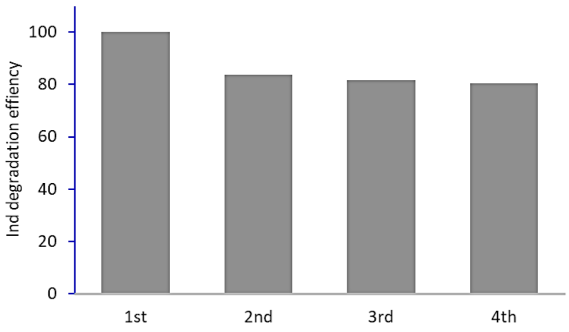


Figure. 7: The efficiency of Ind degradation by H_2O_2 catalyzed by $Fe_2V_4O_{13}$ in four runs. Reaction conditions: m($Fe_2V_4O_{13}$) = 3 mg (on 200 mg of zeolite 4A); $[Ind]_o$ = 0.1 mM; $[H_2O_2]_o$ = 0.3 mM; pH 4; T = 298 K

Preliminary evaluation of the heterogeneous Fenton-like system on treating oil-and-grease polluted wastewater

The critical input parameter of oil-and-grease polluted wastewater is COD. The average COD value before the treatment was 2350 mg/L. After treating the wastewater, the mixture reaction was stopped by removing the catalyst. The COD value after treating was 1150 mg/L. The mean COD removal efficiency is 51 % after 2 hours. It can be improved by optimizing the oxidation reaction conditions, such as the concentration of hydrogen peroxide, the ratio of catalyst and hydrogen peroxide, and the pH of the reaction mixture.

Conclusion

In our study, the conditions for the preparation of catalytic complex oxide, $Fe_2V_4O_{13}$ were investigated, and the optimal parameters were given. In terms of the catalytic activity, the material synthesized at 80°C in 10 hours and annealed at 500 °C in 5 hours is better than the others. The catalyst also presented stability during its catalytic action. This material indicates a promise for the treatment of wastewater containing different organic compounds such as dyes or hydrocarbons using heterogeneous Fenton-like reagents. For further application, the optimal conditions for oily wastewater treatment should be investigated.

Acknowledgments

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