Studies on Catalytic Activity of Nanostructure Mn_2O_3 Prepared by Solvent-thermal Method on Degrading Crystal Violet

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Abstract

Nanostructure manganese oxide shows very good catalytic activity in waste water treatment of dyeing industry. A few nano manganese oxides are prepared through different methods, Their catalytic degradation property of dyeing material (crystal violet solution) is tested with H_2O_2 as oxidizer. Besides, the influence of other parameters are also studied, including catalyst dosage, H_2O_2 dosage and catalyst circulation. After reaction of 60 minutes, degradation of crystal violet can reach over 99% for most catalyst samples.

Keywords: Nanostructure, Mn_2O_3, Catalytic activity, Degradation property, Crystal violet

1. Introduction

Environment problems are increasing today, in which the dispose of industrial wastewater is one of the most important. And dyeing wastewater is a typical example of such industrial wastewater. Nano material is one of the most revolutionary material for its unique properties brought by its scale. It is proved its promising application in catalyst industry and manganese oxide is one of the most widely applied nano catalyst[Nie L J, 1997, p45-46; Deepak B A, 2005, p78-87; Wu Z B, 2007, p488-494.]. Manganese oxides have been widely applied as catalyst in waste water treatment, which are a series of complicated oxides, including MnO, MnO_2, Mn_2O_3, Mn_3O_4 etc.[Steven L S, 1999, p123-132.]. Porous manganese oxides materials have different structure from micropore to mesopore due to various preparation methods, chemical composition and crystal structure, which concludes its excellent property of cation exchange, molecular adsorption, oxidation, chemical and magnetic reducibility, etc.[T OZhkuu, 1990, p769-774.]. Therefore, it's widely used in heterogeneous catalysis, toxic wastewater treatment, dye wastewater degradation etc.[Yang Z H, 2006, p679-684.]. The aim of this paper is to synthesize catalyst with high catalytic performance and excellent circulation performance with usual methods.

2. Experimental

2.1 Sample preparation

The solution are prepared by adding 30mL 1mol/L manganese sulfate solution into 100mL 0.1mol/L potassium permanganate solution, pH is adjusted to 9-11 with ammonia water, the solution is stirred and shifted into high pressure reactor with teflon coat inside. Then the reactor is heated in an oven at 160℃ for 10 hours, and then cooled to room temperature and filtrated to get the residual. The residual is washed with deioned water and dried in an oven at 60℃ for 10 hours. The residual is ignited for 5 hours in muffle of 300℃; treated with 2mol/L H_2SO_4 for 2 hours at 85℃, and then dehumidified at 80℃ for 20 hours. The sample got by above method is marked C1.

C2 Sample is prepared with 0.180g potassium permanganate, 20g urea and 8.5714g choline chloride. The

potassium permanganate is grinded before well mixed with urea and choline chloride. The mixture is put into high pressure reactor with teflon coat inside, and heated in oven for 10 hours at 160℃. The rest of preparation procedure is same as C1.

Preparation of C3 sample is the same as C2, and the only difference is that 10mL water is added to the mixture when being put into high pressure reactor.

2.2 Synthesis method

The samples are analyzed by X-ray diffraction (XRD) using D8 discover with GADDS, Bruker AXS, with Cu-K. Transmission electron microscopy (TEM) images of sample were taken with HITACHI H-7650 transmission electron microscope, suspended the sample in alcohol with ultrasonic wave and dispersed on copper wire mesh, before TEM test.

2.3 Degradation of crystal violet

Catalyst performance of the sample is tested by degrading of 10mg/L crystal violet solution with H_2O_2 as oxidizer in 60 minutes. The absorbance factor of crystal violet solution after catalyst treatment is tested by spectrophotometer to calculate the residual concentration, which indicates the catalyst performance of C1, C2 and C3. The performances also are studied such as catalyst dosage, H_2O_2 dosage and dosing measure, as well as circulation of catalyst, which may have effects on catalyst performance.

3. Results and Discussion

3.1 X-ray Diffraction and TEM Images

The XRD patterns of C1, C2 and C3 are presented in Fig. 1, respectively. They are all avicennite manganese sesquioxide, well crystallized with no impurity compared with standard spectrogram. The broad diffraction peaks show that the size of grain in sample is smaller than normal.

The TEM images of C1, C2 and C3 are presented in Fig. 2, respectively. C3 has smallest particle size, best diffraction, diameter of 10nm and better sphericity. C1 and C2 are agglomerated and also have a nanoscale diameter, C1 around 80 nm and C2 around 50nm.

3.2 Results of Catalytic Degradation

The crystal violet degradation results with different catalysts are shown in Fig.3. Degradation efficiency of C3 reaches 69.24% after only ten minutes, 95.31% after 30 minutes and 99.83% after a hour later, and degrading rate decrease dramatically after ten minutes.

Degradation efficiency of C1 and C2 are 55.22% and 66.18% after 10 minutes reaction, respectively, which reach to the same after 30 minutes and after 1 hour that of each other reach to 98.89% and 98.53%, respectively.

Fig. 4 shows the catalyst performance of C3 at different dosage: 0.2g/L for i, 1g/L for ii and 0.05g/L for iii. 20 minutes degradation efficiency of i, ii and iii are 91.05%, 87.14%, 77.60%, respectively. But final degradation efficiency after 60 minutes of the three test reaches nearly the same around 90%.

The test shows that the degradation efficiency increases with the increasing dosage of catalyst; however, more dosage of catalyst cannot increase efficiency when the dosage reaches a particular value. It's supposed that more dosage of catalyst can increase the degradation rate and efficiency by H_2O_2 being transferred to·OH[Zhang D, 2007, p5400-5406.]; however, over dose of catalyst may also promote side reaction and do not contribute to degrade efficiency.

Fig. 5 shows catalyst performance of C3 at different dosage of H_2O_2: 5 mL H_2O_2 for i; 2mL H_2O_2 for ii and 1mL H_2O_2 for iii. The degradation efficiency of crystal violet reached to 98% after 60 minutes for all three tests. The figure shows that the degradating rate increase with the increase dosage of H_2O_2.

It can be resulted, for the catalysts composed of nano manganese oxide, the degradation efficiency on dye will increase distinctly with more H_2O_2 as the dosage of H_2O_2 is not numerous, and that will increase less with more adding of H_2O_2. When the concentration of H_2O_2 is small, the adding H_2O_2 will increase the concentration of ·OH lead to rapid degradation of dye. And as the concentration of H_2O_2 reached a particular rate, the catalysts cannot transform more H_2O_2 to ·OH and the degradation efficiency on dye will not increase distinctly.

Table 1. shows that the three catalyst performance used to degrade crystal violet based on parallel experiment, in which the dosage of catalysts is 0.1g/L, initial concentration of dye is 10mg/L and H_2O_2 added in is 2ml with mass fraction 4.5%. The reaction lasts 60 minutes.

Usually, catalyst performance will decrease due to intermediate products produced in reaction, which take over

the catalytic active site and make the performance of catalysts decrease(T. OZhkuu, M. Kitagawa and T. Hirayi, 1990). But in this paper, the degradation efficiency of each catalyst remains well and doesn't decrease with the recycling of catalysts. It's supposed that the degrading rate is too high with catalyst of nano maganese oxides to be influenced by intermediate products. While the samplings for measuring dye concentration take off some catalysts and H_2O_2, its effect on test can be neglected because catalysts and H_2O_2 are well-distributed in dye solution.

4. Conclusions

The test shows that all of the three nano maganese oxide samples can degrade crystal violet and C3 has the best performance. The degradation efficiency increases with the dosage of H_2O_2, and remain at a peak when the dosage of H_2O_2 reaches a particular value. The cause may be that the catalysts cannot transform the extra H_2O_2 to ·OH , and on such occasion, dosage increase of neither H_2O_2 nor catalysts could increase the efficiency if the reaction factors don't vary, and on the other hand it may also promote side reaction.

The degradation efficiency can reach 90% in 30 minutes when the crystal violet is degraded by nano manganese oxides, in which C3 has best catalyst performance.

Based on the above experiment and investigation on the catalyst, it is concluded that nano manganese oxides can be widely applied to treatment organic waste water.

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Table 1. Effect of catalyst recycling

Sample	Degradation of Crystal Violet			
	1st	2nd	3rd	4th
C1	98.89%	94.13%	95.18%	93.83%
C2	98.54%	95.47%	93.33%	92.25%
C3	99.83%	96.01%	94.47%	95.67%

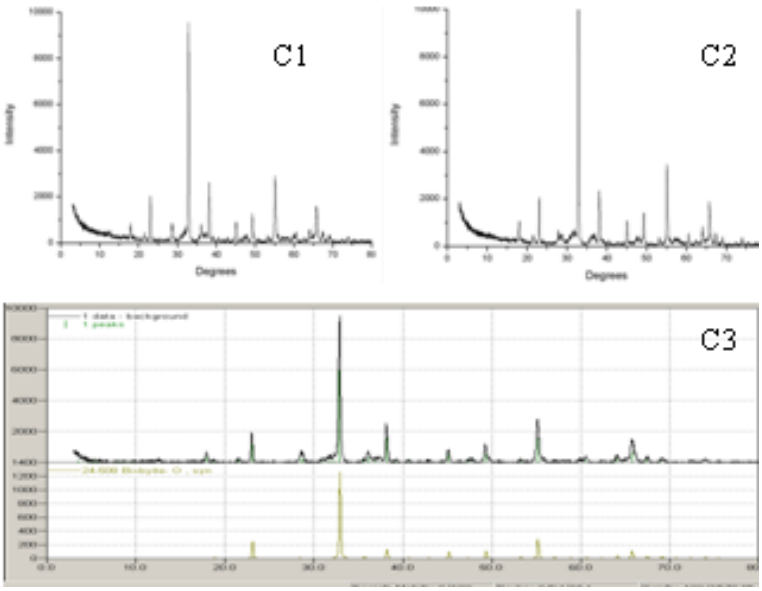

Figure 1. XRD patterns of samples

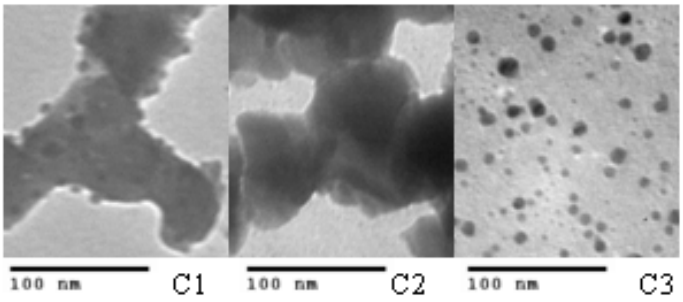

Figure 2. TEM images of samples

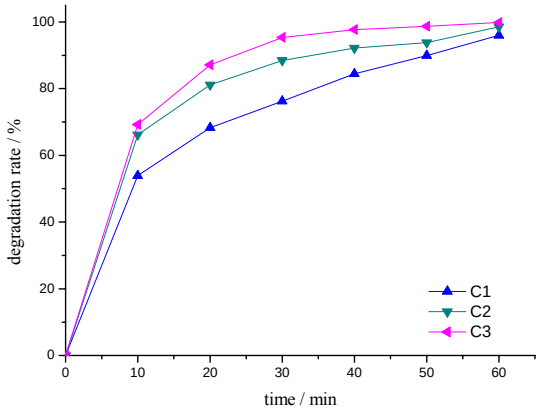

Figure 3. Catalytic Activity of sample

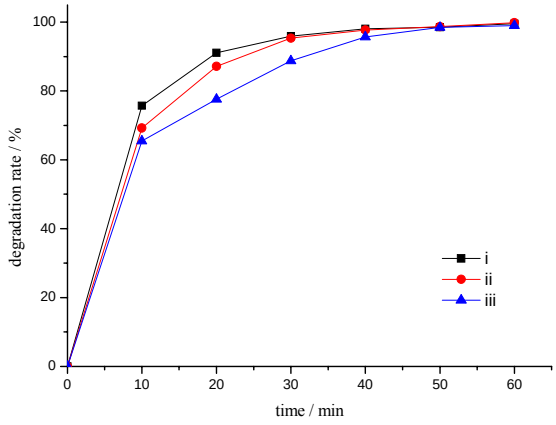

Figure 4. Effect of catalyst dosage

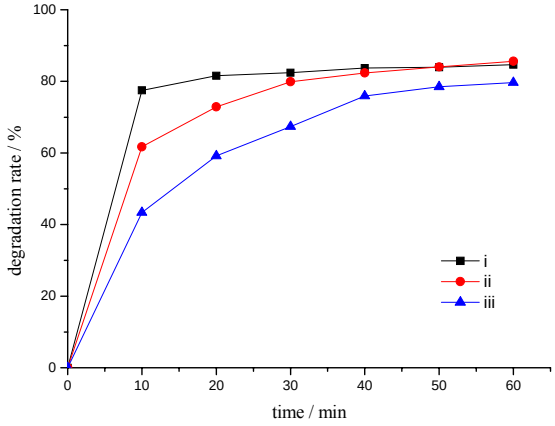

Figure 5. Effect of H_2O_2 dosage