Preparation of Diatomite Supported Nano Zinc Oxide Composite Photocatalytic Material and Study on its Formaldehyde Degradation

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Abstract. This experiment used zinc nitrate as precursor, ethanol as solvent and polyethylene glycol as dispersant, diatomite as carrier, diatomite loaded nano Zinc Oxide was prepared by sol-gel method, in addition, the formaldehyde degradation was studied by two kinds of experimental methods: preparation and loading, preparation and post loading, The samples were characterized by SEM, XRD, BET and IR. Experimental results showed that: Diatomite based nano Zinc Oxide had a continuous adsorption and degradation of formaldehyde, formaldehyde gas with initial concentration was 0.7mg/m^3, after 36h degradation, the concentration reached 0.238mg/m^3, the degradation rate reached to 66%.

1. Introduction

Nano Zinc Oxide was a n type semiconductor[1]. Because of the separation efficiency of photogenerated electrons and holes of nano Zinc Oxide was higher than TiO_2, therefore, nano Zinc Oxide had better photocatalytic activity than TiO_2[2], the formaldehyde could be degraded into harmless gas at normal temperature and pressure, and no pollution could be caused by two times, moreover, the temperature range required by photocatalysis was wide and the cost was low, it had some potential applications in air purification, and had a better prospect in environmental control[3], But nano Zinc Oxide because of nano particles was poor dispersion and difficult to fix and so on, if it was directly applied to the paint coating interior walls, it was easy to fall off, Diatomite which had large particle and strong adsorbability, could be used as the carrier of nano Zinc Oxide, it could can overcome the defects of uneven dispersion and have better photocatalytic effect[4-5].

2. Experiment process

2.1 Main experimental materials and equipments

Materials included: diatomite (Changbai County in Jilin province), six zinc nitrate (AR) and citric acid (AR); polyethylene glycol 6000; ethanol; equipments included: HY-1600 used high temperature energy-saving furnace, DF-101S heat constant temperature type magnetic stirrer, WD-9415B type ultrasonic cleaner, TM3030 SEM、X-Ray Diffractometer System 554800、VC-Sorb 2800TP specific surface and aperture analyzer、IRAffinity-1，the formaldehyde degradation of the environment the cabin was made of organic glass laminated, fully enclosed, volume was about 1m^3, the carrier coated composite powder for frosted glass, effective area was 0.25m^2.

2.2 Preparation of diatomite supported nano Zinc Oxide

Zinc nitrate and citric acid in the mixture of 20:1 and 100mL in deionized water, stirred evenly, ethanol of 10ml was put slowly, diatomite was added under the 2:1 ratio of zinc nitrate with diatomite then ultrasonic treatment for 30min; the suspension was obtained in flask, added trace amount of polyvinyl alcohol, magnetic mixed 6h, static 6h, filtration, dried, grinded, under 600℃ roasted 2h, preparation of diatomite supported nano composite photocatalytic materials Zinc Oxide powder called A; Zinc nitrate and citric acid by 20:1 mixed with 100mL deionized water, evenly stirring, ethanol of 10ml was put slowly, then ultrasonic treatment for 30min, the suspension into the flask, magnetic stirring after 5h by zinc nitrate and diatomite was added under the 2:1 ratio of zinc nitrate with diatomite and trace polyvinyl alcohol, continue stirred 1h static 6h, filtration, dried, grinded, under 600℃ roasted 2h, preparation of diatomite supported nano composite photocatalytic materials Zinc Oxide powder called B.

2.3 Formaldehyde degradation

Formaldehyde degradation experiment: firstly, the formaldehyde adsorption experiment in the reaction cabin (such as Figure 1) was carried out to overcome the error of the following experiment. Then, the diatomite based nano Zinc Oxide sample coated on the glass. Formaldehyde initial concentration of 0.7mg/m^3 was injected into reaction chamber, residual formaldehyde gas concentration was measured every 5h, adsorption degradation time-formaldehyde concentration curve was made .

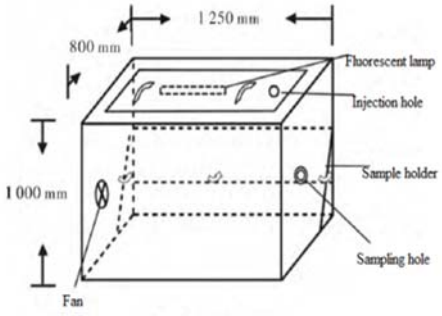

Figure 1. Degradation of formaldehyde gas reaction chamber.

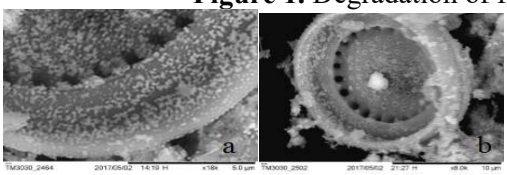

Figure 2. SEM of composite photocatalytic material powder A (a、b).

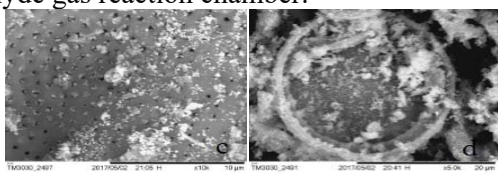

Figure 3. SEM of composite photocatalytic material powder B (c、d).

3. Experimental results and analysis

3.1 Morphology analysis of the sample

Figure 2 and 3 were SEM of composite photocatalytic material powder A and B. the distribution of nano Zinc Oxide on diatomite was observed, part of the grain size distribution was dense, the existence of large granular aggregate amount of nano particles, founded that Zinc Oxide of composite photocatalytic material powder A was dispersed, the Zinc Oxide dispersion of composite photocatalytic material powder A was better than the nano particles in Figure 3. As can be seen from the SEM, there was no obvious change in the morphology of the nano Zinc Oxide of composite photocatalytic material powder A compared with B, just the dispersion was better and the particle size was uniform. The preparation method of diatomite supported nano Zinc Oxide should be prepared by the method of preparation and loading.

3.2 X ray diffraction analysis

Figure 4 and 5 were the XRD spectra of composite photocatalytic material powder A and B, the composite photocatalytic material powder A had a certain change compared with the composite photocatalytic material powder B. In Figure 3 and 4, the diffraction peak at 2 theta to 28° was SiO_2, 2 theta was 31°, 38° and 56°, the diffraction peak was ZnO, and the peaks in the XRD diagram were very strong and sharp, and there was no other impurity peak, which showed that the purity of the sample was very high. X ray diffraction peak intensity of samples was strong, due to the different preparation methods of diatomite supported nano Zinc Oxide to internal lattice changes, the intensity of diffraction peak that load after the preparation higher than preparating and loading.

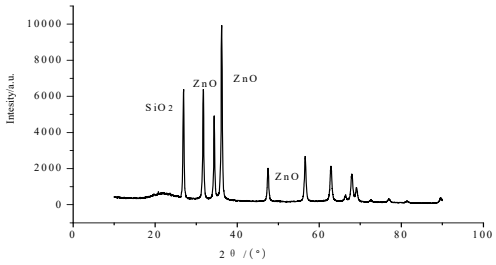

Figure 4. XRD of Composite Photocatalytic Material Powder A.

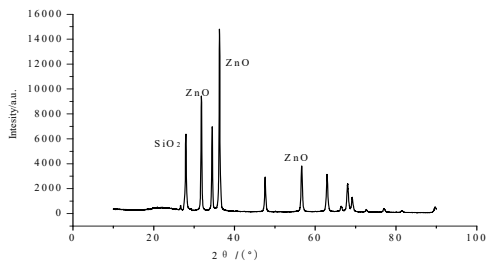

Figure 5. XRD of Composite Photocatalytic Material Powder B.

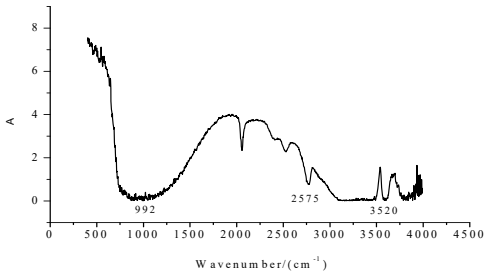

Figure 6. IR of Composite Photocatalytic Material Powder A.

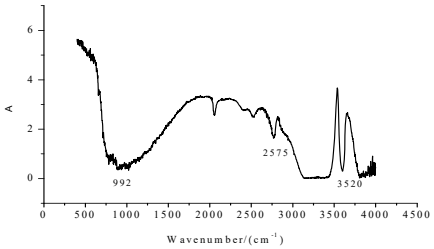

Figure 7. IR of Composite Photocatalytic Material Powder B.

3.3 Study on formaldehyde degradation of samples

Table 1 was the specific surface area and average particle size of the diatomite supported nano Zinc Oxide composite photocatalyst composite powder A and B, from that: because the nano particles increased, the surface area was greatly increased, average particle size decreased, diatomite as a carrier of nano Zinc Oxide particles, in photocatalytic process, and the contact area with formaldehyde molecule will be bigger, so as to improve the formaldehyde degradation.

Table 1. Specific surface area and average particle size of sample.

Sample	Specific surface area□m^2/g□	Average particle size□nm□
Diatomite	14.56	9.2
Composite powder A	45.56	5.1
Composite powder B	40.23	5.3

3.4. Infrared analysis of samples

The infrared spectra of the sample were shown in Figure 6 and 7, From that: there were O-Si-O symmetric stretching vibration bands and O-Si-O asymmetric stretching vibration bands in the range of 900~1200cm-1. There was an obvious absorption peak at 992cm-1. It was the asymmetric stretching vibration of Si-O-Zn. It showed that the bonding between Zinc Oxide and diatomite occurs during the preparation process, formed Si-O-Zn bond. In the range of 3500~3600cm-1, it was the position of hydroxyl vibration, indicated the expansion of the structure water and the adsorbed water,

and the vibration peak of the composite photocatalytic material powder B was obviously increased, indicated that the hydroxyl content was very high in the sample. With XRD analysis and SEM images, it can be concluded that most of the Zinc Oxide particle load to the surface and pores of diatomite.

3.5. Study on formaldehyde degradation of samples

From figure 8, the initial concentration was 0.7mg/m^3 formaldehyde gas in the reaction chamber after 3h can be reduced to 0.6mg/m^3. From the curve: the reaction tank on adsorption of formaldehyde gas saturation concentration was about 0.1mg/m^3, so during the formal experiment the concentration of formaldehyde gas were increased in 0.1mg/m^3 based.

From Figure 9, during 9h, formaldehyde concentration decreased rapidly; then, the formaldehyde concentration decreased slowly, because the initial concentration of formaldehyde was higher, the formaldehyde was rapidly adsorbed by sub micropores of diatomite; With decreasing concentration of formaldehyde in the reaction chamber, adsorption of diatomite to formaldehyde reached equilibrium. In fluorescent light irradiation, inspired Zinc Oxide to produce highly active nano hole electron pairs, the high activity of electron hole pair would take electronics of O_2 and H_2O around and its generated strong oxidation ·OH、$\cdot O_2^-$, reached the purpose of formaldehyde degradation. Diatomite composite photocatalyst powder A and B after the adsorption and degradation of 36h, the formaldehyde degradation rate were 29%, 64.6%, 51.7%, indicated that the adsorption of formaldehyde on single diatomite belonged to physical adsorption, while the preparation and loading than the loaded after the preparation of formaldehyde degradation rate was 12.9%. Because Zinc Oxide nano composite photocatalyst B powder agglomerate phenomenon, generated ·OH、$\cdot O_2^-$was less, so the formaldehyde degradation rate was low.

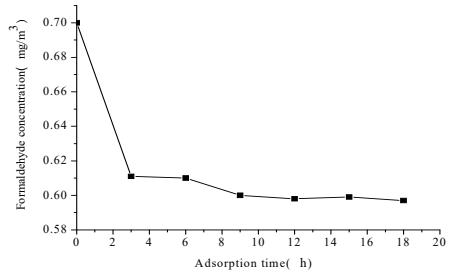

Figure 8. Formaldehyde adsorption of reactor.

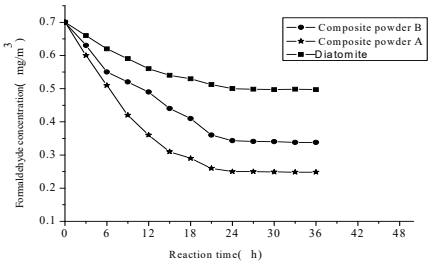

Figure 9. Adsorption and degradation of formaldehyde of sample.

4. Conclusion

Composite photocatalyst material powder was prepared by sol-gel method using diatomite as a carrier, Zinc Oxide as photocatalytic materials, the experimental method was by preparing and loading, composite powders were dispersed uniformly and the specific surface area was 45.56 m^2/g, the average particle size was 5.1nm. After 36h the degradation of formaldehyde rate reached to 64.6%, 37% higher than the single diatomite adsorption.

Acknowledgments

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