Hindawi Publishing Corporation
Journal of Chemistry
Volume 2015, Article ID 806568, 7 pages
http://dx.doi.org/10.1155/2015/806568

Research Article

Preparation and Photocatalytic Properties of TiO_2-Al_2O_3 Composite Loaded Catalysts

Jianzhong Pei,[1] Weisi Ma,[1] Rui Li,[1] Yanwei Li,[2] and Hongzhao Du[3]

[1]*School of Highway, Chang'an University, Xi'an, Shaanxi 710064, China*
[2]*Transport Agency of Shijiazhuang, Shijiazhuang, Hebei 050001, China*
[3]*Henan Provincial Communications Planning Survey & Design Institute Co., Ltd., Zhengzhou, Henan 450052, China*

Correspondence should be addressed to Jianzhong Pei; peijianzhong@126.com

Received 11 August 2014; Revised 30 November 2014; Accepted 21 December 2014

Academic Editor: Kaustubha Mohanty

This paper presents an experimental approach to study catalytic effects of Fe^{3+} modified nanometer titanium dioxide (TiO_2) loaded on aluminium oxide (Al_2O_3). Sol-gel method was used to prepare modified TiO_2 loaded on carrier. Purification tests were conducted in a self-developed instrument to study catalytic effects of TiO_2 loaded on Al_2O_3 with different contents through degradation rate. The modification mechanism was studied by scanning electron microscope (SEM). Results showed that loading on Al_2O_3 improved photocatalytic effect of TiO_2 modified with Fe^{3+}. The best photocatalytic effect was achieved under catalytic action of Al_2O_3 loaded with 10% TiO_2 composite; the degradation rates were 6.9%, 13.8%, 21.4%, and 49.2%, respectively, 0.7%, 3.9%, 1.3%, and 15.1% larger than unloaded TiO_2. SEM results of four catalysts showed that nanometer TiO_2 was coated in form of grain on the surface of Al_2O_3. The optimal loading content was 10% at which the nanometer TiO_2 grains were coated on the surface of Al_2O_3 uniformly.

1. Introduction

There was a lot of automobile exhaust in the highway tunnels. This exhaust contained a lot of gas phase carbon monoxide (CO), nitrogen oxide (NO_X), hydrocarbons, and other pollutants [1]. Meanwhile, the harmful gas inside tunnels was hard to be expelled, especially in long tunnel encountering long time traffic jams, which would seriously influence driving safety and personnel health [2]. Therefore, it was necessary to reduce harmful gas in tunnels, especially in long tunnel. Semiconductor optical catalyst which emerged in the 1970s was a new oxidation technology, showing good function for degradation of organic pollutants [3]. TiO_2 powders as a kind of photocatalytic materials had been successfully applied in pollutant disposal, especially in sewage treatment and indoor waste gas purification, and certain achievements have been made [4, 5]. However, disadvantages were also shown in actual application. For example, the TiO_2 was difficult to precipitate and recover due to its tiny particles, during which the active ingredient was lost by a large percentage [6].

In order to solve the problems above, a considerable number of research efforts have been made. At present, photocatalytic materials fixed to a carrier had become a current trend. Nanometer TiO_2 particle fixed on montmorillonite showed better photocatalytic property, because specific surface area of the nanometer TiO_2 became bigger when loaded on carriers such as diatom class [7, 8], montmorillonite [9, 10], and kaolinite [11–13], so as to increase utilization rate of the light and absorption ability of pollutants. In addition, a few carriers such as metal chemicals could interact with nanometer TiO_2 particles, and this interaction was helpful for separation of the electronic hole of nanometer TiO_2 particles, which could improve the catalytic effect [14]. However, these researches were mainly used for waste water treatment; few studies were conducted in the aspect of gas purification in tunnels. Therefore, the goal of this paper was to (1) research catalytic efficiency of nanometer TiO_2 loaded on Al_2O_3 for major kinds of gases in tail gas and (2) study modification mechanism of the composite materials.

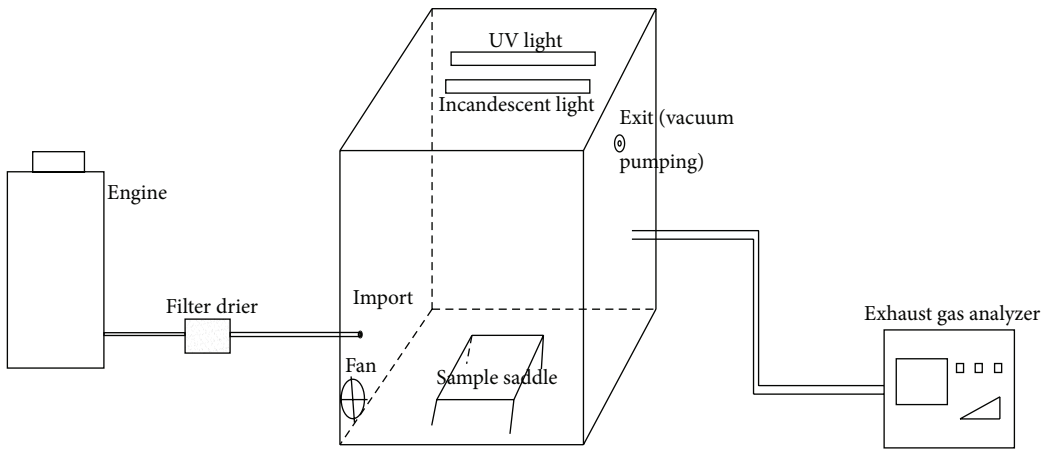

Figure 1: Equipment for exhaust gas purification.

2. Experimental

2.1. Preparation of Photocatalytic Materials. Modified nanometer TiO_2 was prepared by sol-gel method. (1) Prepare TiO_2 sol doped with 0.1% Fe^{3+}, used as control sample; (2) prepare Al_2O_3 saturated solution with a certain amount of alumina and deionized water; (3) the wet gel composed of TiO_2 sol and Al_2O_3 saturated solution was prepared by a 30-minute violent mixing; (4) dry gel was obtained by drying the wet gel in vacuum at 80°C. (5) TiO_2 loaded on Al_2O_3 was obtained by calcination at 500°C in a muffle furnace for 2 hours.

Four catalysts were prepared by the above procedures, namely, catalyst 1, catalyst 2, catalyst 3, and catalyst 4, respectively. The details of the catalysts are shown in Table 1.

2.2. Test Instruments and Methods

2.2.1. Test Instruments. A set of test equipment for exhaust gas purification was developed to conduct purification experiments (see Figure 1). The test equipment was composed of motorcycle engine, filter and reaction tank, and an AVL-4000 exhaust gas analyzer (parameters are shown in Table 2). There were inlet control valves in the lower part of reaction tank, and the exhaust port was wetted in the upper portion of the test equipment. To simulate the natural wind in tunnel, a fan was located in the lower side. Sample bracket for test board coated with photocatalytic materials was located in the bottom. A filter filled with material was installed to prevent dust flowing into the reaction tank. Two kinds of light sources, respectively, ultraviolet (UV) light with a wavelength of 287.5 nm and incandescent light similar to the light in tunnels with a wavelength of 500~700 nm were used in this text.

2.2.2. Test Method. Photocatalytic materials produced by sol-gel method were evenly daubed on an organic glass board. The board was 300 mm × 300 mm in length (shown in Figure 2). The board daubed with photocatalytic materials was put into the homemade exhaust catalytic reaction equipment. Purification tests were conducted under the two kinds of light sources when the initial concentration was steady. In this text, degradation rate was calculated and used as evaluation index for catalytic property. Concentrations of HC, CO, CO_2, and NO_X were measured and used to calculate concentration rate with the following equation:

$$\eta = \frac{C_0 - C_1}{C_0} * 100\%, \quad (1)$$

where η was the degradation rate; C_0 was initial concentration; C_1 was concentration in the end of tests.

Figure 2: Sample board for purification test.

Table 1: Four catalysts prepared in this study.

Catalyst type	Notes
Catalyst 1	TiO_2 doped with 0.1% Fe^{3+}, as the control
Catalyst 2	Al_2O_3 loaded with 5% catalyst 1
Catalyst 3	Al_2O_3 loaded with 10% catalyst 1
Catalyst 4	Al_2O_3 loaded with 15% catalyst 1

Table 2: Parameters of AVL-4000.

Gas type	HC (ppm)	CO (%)	CO_2 (%)	NO_X (ppm)
Testing range	0~20000	0~10	0~20	0~5000
Accuracy	1	0.01	0.1	1

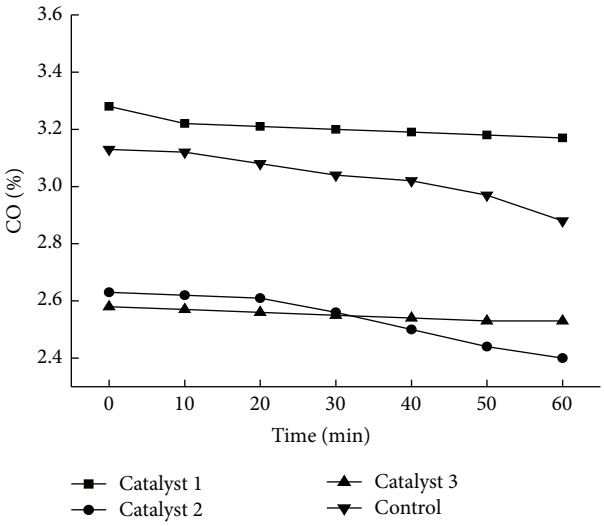

Figure 3: Degradation rate of CO under catalytic action of different catalysts.

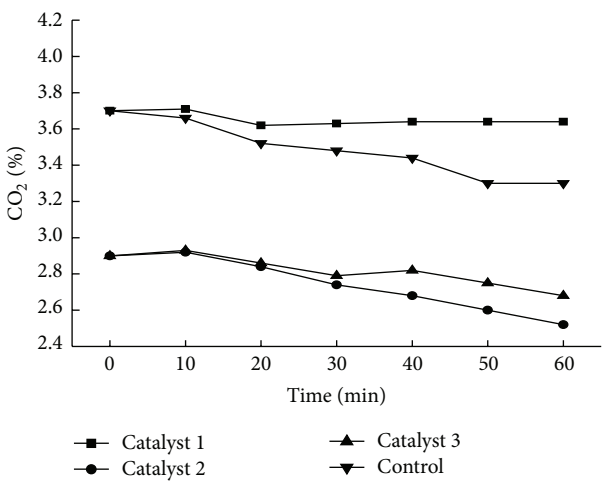

Figure 4: Degradation rate of CO_2 under catalytic action of different catalysts.

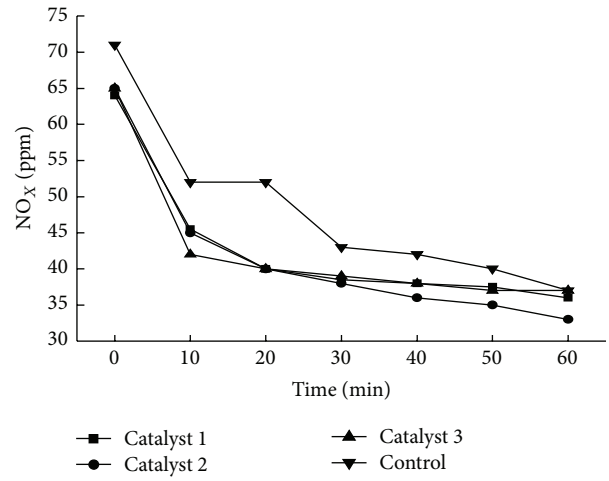

Figure 5: Degradation rate of NO_X under catalytic action of different catalysts.

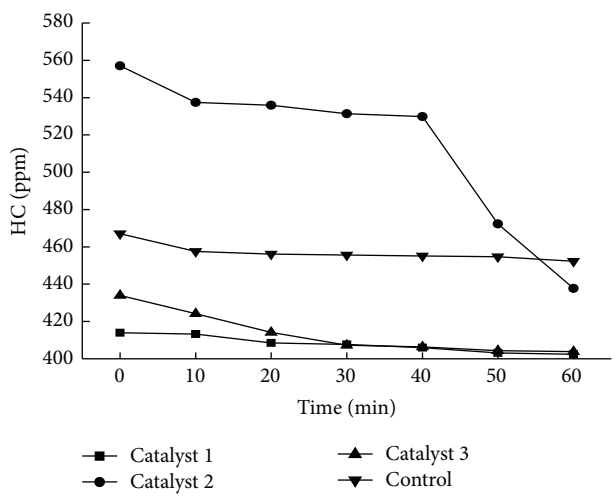

Figure 6: Degradation rate of HC under catalytic action of different catalysts.

3. Results and Discussion

3.1. Catalysis of Ultraviolet Light. The initial concentrations of CO, CO_2, NO_X, and HC were recorded after concentration in reaction tank was steady. Test data were measured every 10 min; concentrations of CO, CO_2, NO_X, and HC versus time during 60 min were plotted in Figures 3–6. Figures 3–6 represent concentration change of the four gases under catalytic action of unmodified TiO_2 and TiO_2 loaded on Al_2O_3 with different contents. The differences shown in each figure represent catalytic action of TiO_2 loaded on Al_2O_3. It was found that

(1) change of CO and CO_2 concentration was not apparent, it was mainly because a series of complex REDOX reactions happened under the effect of catalyst between CO and CO_2, and these reactions were reversible chemical reactions in which CO and CO_2 acted as reactant and products for each other;

(2) concentration of HC declined with the increase of action time and it was mainly because HC was decomposed into water and carbon oxide;

(3) there was notable decline in concentration of NO_X especially in the first 30 minutes. This is mainly because NO_X was oxidized into HNO_3 and H_2O under the action of catalyst.

The quantitative impacts of Fe^{3+} on the catalytic effects of TiO_2 are plotted in Figure 7. Degradation rates of four gases were calculated according to data obtained from purification tests and (1). The following findings were observed.

(1) In general, doping Fe^{3+} improved the photocatalysis efficiency of nano-TiO_2.

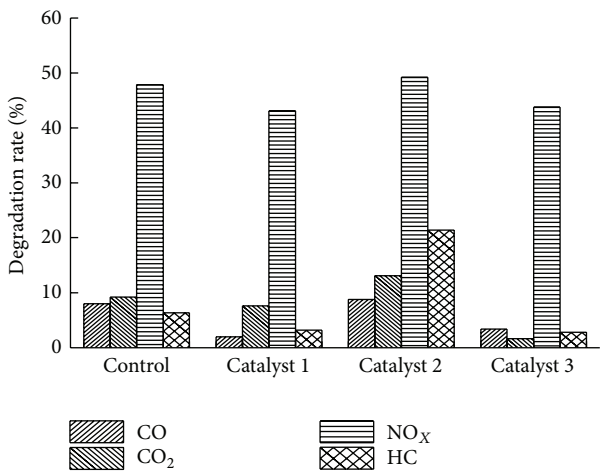

Figure 7: Degradation rates of CO, CO_2, NO_X, and HC under catalytic action of different catalysts.

(2) Catalytic effect of catalyst 3 was the best, with degradation rate of CO, CO_2, HC, and NO_X, respectively, 6.9%, 13.8%, 21.4%, and 49.2%, increased by 0.7%, 3.9%, 1.3%, and 15.1% compared to TiO_2 unloaded on Al_2O_3.

(3) Compared with the catalysis of catalyst 1, the degradation rates of the four gases under the catalysis of catalyst 2 and catalyst 4 were reduced. Therefore, catalyst loaded on Al_2O_3 had a significant influence on the catalysis effect. Too high or too low content would reduce the effect of the catalyst. The optimal dose was suggested to be controlled at about 10% in this paper.

3.2. Catalysis of the Incandescent Light. The optimal dosage of carrier was obtained at present. Therefore TiO_2 loaded on the optimal dosage of 10% Al_2O_3 was used to study catalytic effect under natural light in tunnels. To this end, purification experiments were performed under incandescent lamp light, and concentration changes of CO, CO_2, NO_X, and HC are, respectively, plotted in Figures 8–11. Each curve in Figure 8 represents concentration change of CO under catalytic action of catalyst 1 and catalyst 3 in natural light condition. It could found that, under incandescent lamp light condition, concentration of CO, CO_2, HC, and NO_X decreased as testing time increased, especially in the action of catalyst 3. Degradation rates of four components of exhaust were, respectively, 1.9%, 2.3%, 5.1%, and 27.8% under the catalytic action of catalyst 3, 0.6%, 0.6%, 2.3%, and 8.2% larger compared to degradation rate under catalyst 1.

To observe quantitatively the impact of Al_2O_3 on the purification, degradation rates of four components of exhaust were calculated according to (1) and plotted in Figure 12. It could be found that (1) with catalytic action of catalyst 1, compared to catalytic effect under UV light, degradation rates of four gases were decreased by 8.0%, 10.8%, 6.9%, and 20.1%, mainly because the wavelength range of UV is easier to activate TiO_2 and (2) with catalytic action of catalyst 3, compared to catalytic effect under UV light, degradation rates of four gases were decreased by 6.1%, 8.5%, 1.8%, and 0%, respectively. It could be concluded that Al_2O_3 weakened light source sensitivity of TiO_2.

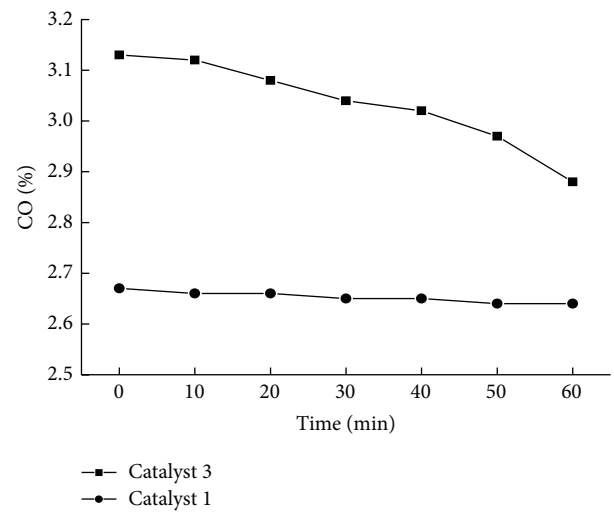

Figure 8: Concentration of CO versus time under catalytic effect of catalyst 1 and catalyst 3, respectively.

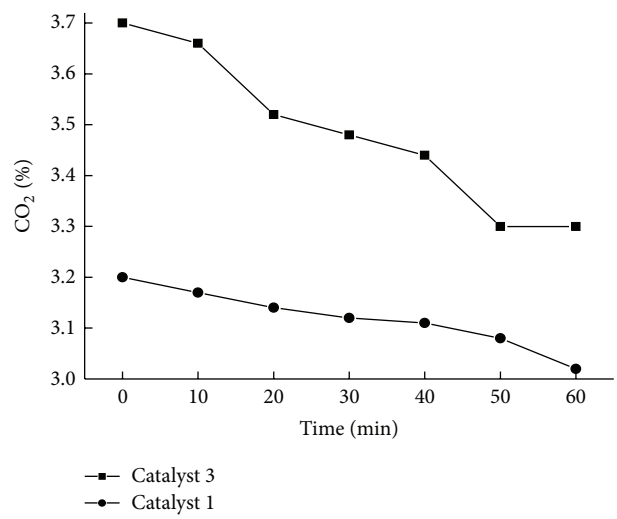

Figure 9: Concentration of CO_2 versus time under catalytic effect of catalyst 1 and catalyst 3, respectively.

3.3. Analysis of Catalytic Process Using GCMS and XRD. Carrene was used to collect exhaust for 20 minutes. Then the collected exhaust was concentrated by the nitrogen concentration instrument. This first group is the liquor before being catalyzed. As a contrast test, exhaust was collected and then was put in the equipment for exhaust gas purification, and, after 20 minutes, the liquor was taken out and was concentrated by the nitrogen concentration instrument. This second group is the liquor after being catalyzed. Then the first group and second group were tested by GC.

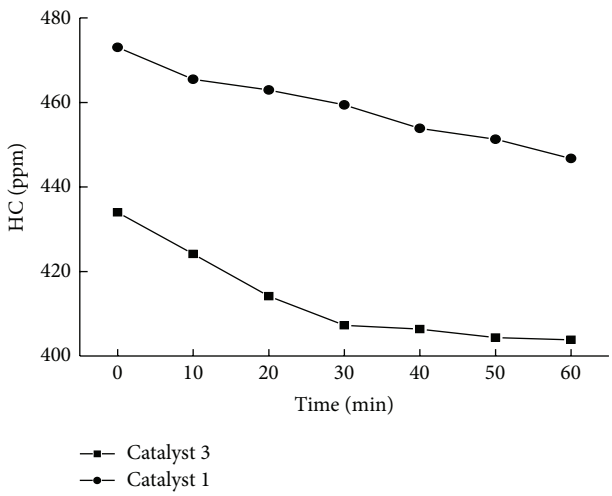

Figure 10: Concentration of NO_X versus time under catalytic effect of catalysts 1 and 3, respectively.

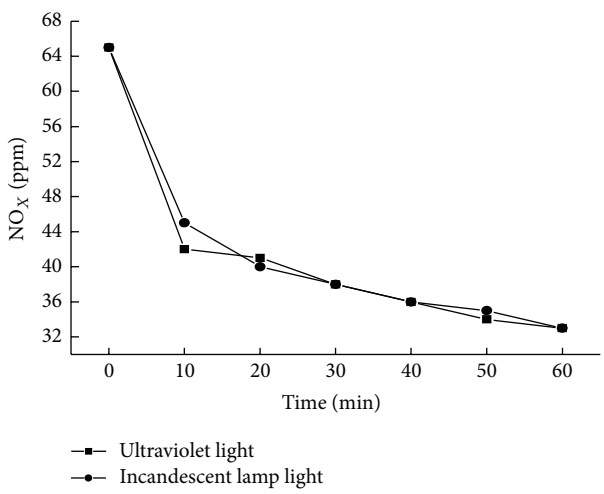

Figure 11: Concentration of HC versus time under catalytic effect of catalysts 1 and 3, respectively.

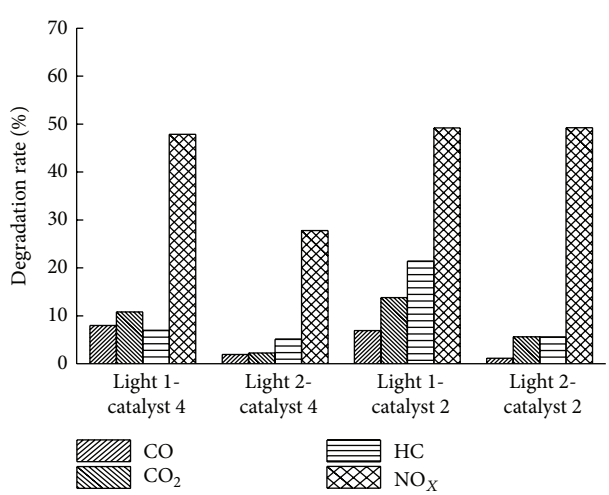

Figure 12: Degradation rates of CO, CO_2, HC, and NO_X under photocatalytic action of catalyst 4 and catalyst 2, UV light and ordinary light condition, respectively.

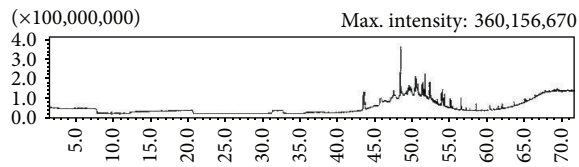

Figure 13: Total ionic chromatogram of automobile exhaust.

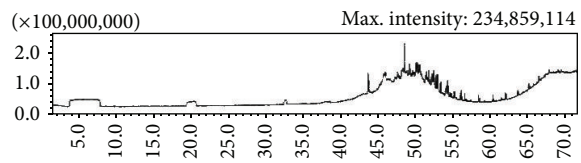

Figure 14: Total ionic chromatogram of automobile exhaust after using catalyst.

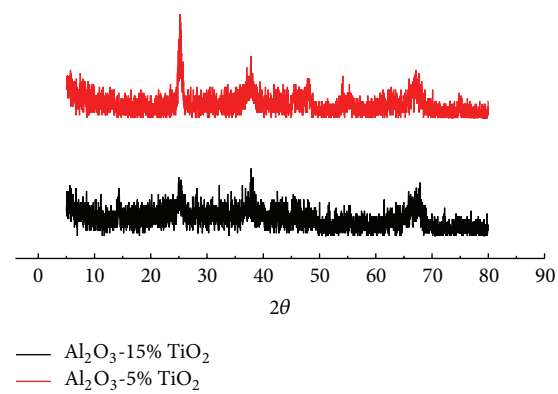

Figure 15: XRD of catalysts 2 and 4, respectively.

Total ionic chromatogram of automobile exhaust before and after using catalyst is shown in Figures 13 and 14, respectively. According to Figures 13 and 14, it can be found that most of automobile exhaust concentration has dropped after using catalyst, which can explain that using catalyst can work on reducing automobile exhaust.

X-ray diffraction (XRD) of catalysts 2 and 4 is shown in Figure 15. According to Figure 15, it can be found that XRD of two kinds of catalysts is similar. The diffraction peak intensity and width of two kinds of catalysts are different. TiO_2 nanoparticles exist on Al_2O_3 in the form of particles. Doped Al_2O_3 inhibits the growth of TiO_2 grains. The specific surface area of TiO_2 nanoparticles increased, so both adsorption capacity and catalytic ability are enhanced. The average particle size of TiO_2 nanoparticles prepared is 15.2 nm and nano-TiO_2 prepared is anatase phase, so it has higher catalytic efficiency.

3.4. Analysis of Modification Mechanism. Photocatalytic reaction rate was closely related to many factors such as catalyst characteristics, system composition, and reactant type. Generally speaking, catalyst features such as TiO_2 crystal structure and lattice [15], TiO_2 particle size [16], and electronic defects and hole capture agent had a decisive

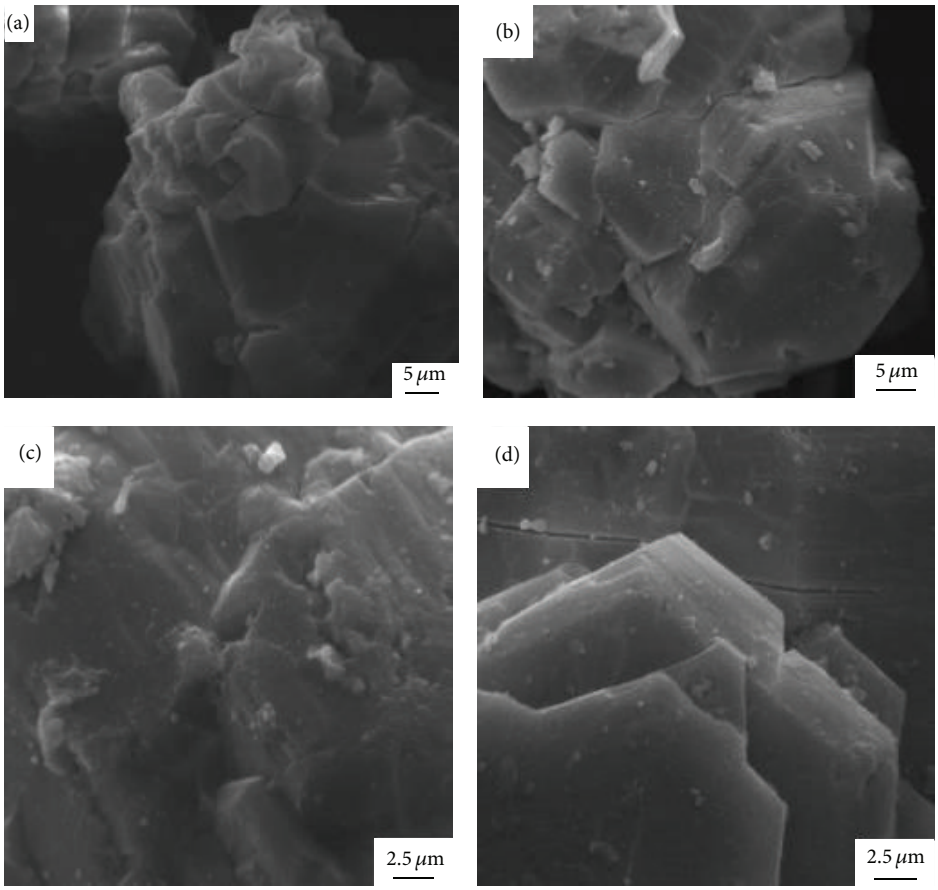

Figure 16: The SEM picture of TiO_2-Al_2O_3 composite.

influence on the light-catalyzed role of TiO_2 [17]. Quanta 200 scanning electron microscope instrument made by FEI was used to make crystal analysis of TiO_2-Al_2O_3 composite, in purpose of analyzing modification mechanism of TiO_2 composite loaded on Al_2O_3. Parameters of scanning electron microscope instrument were set as follows. Speed up voltage was 20 Kv, and magnification was 10000 times. SEM of modified and unmodified TiO_2 is plotted in Figure 16.

It could be seen from the scanning electron microscope pictures that there was obvious synergistic reaction between nanometer TiO_2 and active Al_2O_3 grains. Nanometer TiO_2 were coated in the form of grain with particle size ranging from 10 to 20 nm on the surface of Al_2O_3 [18]. Figure 16(a) shows the SEM of Al_2O_3 calcining sample; it could be found that surfaces of Al_2O_3 were smooth. Figure 16(d) shows the SEM picture of Al_2O_3 loaded with 5% TiO_2. In this figure, the surfaces of the Al_2O_3 were only coated with a handful of TiO_2 grains, because content of TiO_2 particles was insufficient to cover the surface of Al_2O_3. Figure 16(c) shows the SEM picture of Al_2O_3 loaded with 10% TiO_2. In this picture, the TiO_2 particles were uniformly coated on the surfaces of the Al_2O_3 crystals and the TiO_2 particles kept well hexagonal shapes. These characteristics would accelerate the air pollutants moving to the surfaces of TiO_2 and make a good contribution to the degradation of the contaminants. At the same time, the catabolite would leave the TiO_2 particles quickly. In this way, the catalysis of the TiO_2 particles was ameliorated. Figure 16(b) showed the magnified patterns of the Al_2O_3 loaded with TiO_2 (15%) calcining sample. It could be seen that TiO_2 particles were coated on the surface of Al_2O_3. However, the content of TiO_2 was too large to cause obvious cracks on the surface of Al_2O_3; photogenerated electrons and holes were covered, resulting in negative influence on the catalysis [19, 20].

4. Conclusions

(1) Loading on Al_2O_3 improved photocatalytic effect of TiO_2 modified with Fe^{3+}, and the best purification effect was achieved when the loaded content of TiO_2 was 10%. The degradation rates of CO, CO_2, HC, and NO_X were 6.9%, 13.8%, 21.4%, and 49.2%, respectively, under UV light condition, 0.7%, 3.9%, 1.3%, and 15.1% larger compared to unloaded condition. Under ordinary light condition, degradation rates of the CO, CO_2, HC, and NO_X were 1.1%, 5.6%, 5.6%, and 49.2%, respectively, almost the same as the results in the ultraviolet light condition.

(2) It could be seen from the scanning electron microscope pictures that there was obvious synergistic

reaction between nanometer TiO_2 and active Al_2O_3 grains. Nanometer TiO_2 was coated in form of grain on the surface of Al_2O_3. The optimal loading content was 10%; at this condition, nanometer TiO_2 grains were coated on the surface of Al_2O_3 uniformly.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

[1] Y. Lei, X. Li, Y. Lu, and H. Xiao, "The advance of the treatment of air pollution in road tunnel," *Techniques and Equipment for Environmental Pollution Control*, vol. 6, no. 2, pp. 40–44, 1998.

[2] B.-G. Wang, W.-M. Lǔ, Y. Zhou, M. Shao, and Y.-H. Zhang, "Emission characteristic of PAHs composition in motor vehicles exhaust of city tunnel," *China Environmental Science*, vol. 27, no. 4, pp. 482–487, 2007.

[3] A. Fujishima and K. Honda, "Electrochemical photolysis of water at a semiconductor electrode," *Nature*, vol. 238, no. 5358, pp. 37–38, 1972.

[4] W. Shen, W. Zhao, F. He, and Y. Fang, "TiO_2-based photocatalysis and its applications for waste water treatment," *Progress in Chemistry*, vol. 10, no. 4, pp. 349–361, 1998.

[5] D. Zhang, R. Qiu, L. Song, B. Eric, Y. Mo, and X. Huang, "Role of oxygen active species in the photocatalytic degradation of phenol using polymer sensitized TiO_2 under visible light irradiation," *Journal of Hazardous Materials*, vol. 163, no. 2-3, pp. 843–847, 2009.

[6] W. Haidong, T. Yucai, Z. Hai, and L. I. Hailiang, "Progress in research on TiO_2/layer mineral composite," *Materials Review*, vol. 21, no. 6, pp. 134–137, 2001.

[7] Y.-Y. Su, Y.-Q. Yu, P.-S. Yang, X.-T. Wang, and X.-B. Zhu, "Photocatalytic degradation of anthraquinone dye wastewater with nano-TiO_2/diatomite," *China Environmental Science*, vol. 29, no. 11, pp. 1171–1176, 2009.

[8] X. Yu and H. Wei, "Layer-by-layer assembly of TiO_2 colloids onto diatomite to build hierarchical porous materials," *Advances in Colloid and Interface Science*, vol. 323, pp. 326–331, 2008.

[9] B. Damardji, H. Khalaf, L. Duclaux, and B. David, "Preparation of TiO_2-pillared montmorillonite as photocatalyst Part I. Microwave calcination, characterisation, and adsorption of a textile azo dye," *Applied Clay Science*, vol. 44, no. 3-4, pp. 201–207, 2009.

[10] F. Li, Y. Jiang, M. Xia, M. Sun, B. Xue, and X. Ren, "A high-stability silica-clay composite: synthesis, characterization and combination with TiO_2 as a novel photocatalyst for Azo dye," *Journal of Hazardous Materials*, vol. 165, no. 1–3, pp. 1219–1223, 2009.

[11] M. N. Chong, V. Vimonses, S. Lei, B. Jin, C. Chow, and C. Saint, "Synthesis and characterisation of novel titania impregnated kaolinite nano-photocatalyst," *Microporous and Mesoporous Materials*, vol. 117, no. 1-2, pp. 233–242, 2009.

[12] Z. Lu, M. Ren, H. Yin et al., "Preparation of nanosized anatase TiO_2-coated kaolin composites and their pigmentary properties," *Powder Technology*, vol. 196, no. 2, pp. 122–125, 2009.

[13] V. Vimonses, M. N. Chong, and B. Jin, "Evaluation of the physical properties and photodegradation ability of titania nanocrystalline impregnated onto modified kaolin," *Microporous and Mesoporous Materials*, vol. 132, no. 1-2, pp. 201–209, 2010.

[14] L.-R. Lei, Y.-M. Li, and L.-M. Ma, "Pulping effluent treatment with ozone catalyzed by activated carbon and alumina loaded or unloaded with titanium dioxide," *Journal of South China University of Technology (Natural Science)*, vol. 40, no. 2, pp. 149–155, 2012.

[15] E. Cesca, P. Midrio, R. Boscolo-Berto et al., "Conservative treatment for complex neonatal ovarian cysts: a long-term follow-up analysis," *Journal of Pediatric Surgery*, vol. 48, no. 3, pp. 510–516, 2013.

[16] S. Montieone, R. Thfeu, A. V. Kanaev, E. Scolan, and C. Sanchez, "Quantum size effect in TiO_2 nanoparticles: does it exist?" *Applied Surface Science*, vol. 162-163, pp. 565–570, 2000.

[17] A. V. Emeline, V. Ryabchuk, and N. Serpone, "Factors affecting the efficiency of a photocatalyzed process in aqueous metal-oxide dispersions: prospect of distinguishing between two kinetic models," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 133, no. 1-2, pp. 89–97, 2000.

[18] L.-M. Wang, T. Hang, and L.-T. Huang, "Preparation of composite photocatalyst TiO_2–$A1_2O_3$ and capability of photocatalyst," *Journal of Guizhou University (Natural Science)*, vol. 22, no. 5, pp. 29–31, 2008.

[19] X. R. Yan, W. W. Guo, K. X. Song, M. L. Huo, and J. P. Wang, "Preparation of nano-TiO_2 film on SiO_2 and photocatalytic activity," *Acta Energiae Solaris Sinica*, vol. 22, no. 2, pp. 196–199, 2001.

[20] X.-R. Yan, X.-H. Li, K.-X. Song, H.-T. Zhao, and X.-Z. Chen, "Preparation and characterization of nanometer photocatalysis SnO_2@TiO_2," *Chemical Journal of Chinese Universities*, vol. 22, no. 4, pp. 610–613, 2001.