

Preparation and application of granular ZnO/Al₂O₃ catalyst for the removal of hazardous trichloroethylene

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Received 9 January 2006; received in revised form 26 June 2006; accepted 27 July 2006

Available online 31 July 2006

Abstract

Trichloroethylene (TCE) is a volatile and nerve-toxic liquid, which is widely used in many industries as an organic solvent. Without proper treatment, it will be volatilized into the atmosphere easily and hazardous to the human health and the environment. This study tries to prepare granular ZnO/Al₂O₃ catalyst by a modified oil-drop sol–gel process incorporated the incipient wetness impregnation method and estimates its performance on the catalytic decomposition of TCE. The effects of different preparation and operation conditions are also investigated.

Experimental results show that the granular ZnO/Al₂O₃ catalyst has good catalytic performance on TCE decomposition and the conversion of TCE is 98%. ZnO/Al₂O₃(N) catalyst has better performance than ZnO/Al₂O₃(O) at high temperature. Five percent of active metal concentration and 550 °C calcination temperature are the better and economic preparation conditions, and the optimum operation temperature and space velocity are 450 °C and 18,000 h⁻¹, respectively. The conversions of TCE are similar and all higher than 90% as the oxygen concentration in feed gas is higher than 5%. By Fourier transform infrared spectrography (FT-IR) analyses, the major reaction products in the catalytic decomposition of TCE are HCl and CO₂. The Brunauer–Emmett–Teller (BET) surface areas of catalysts are significantly decreased as the calcination temperature is higher than 550 °C due to the sintering of catalyst materials, as well as the reaction temperature is higher than 150 °C due to the accumulations of reaction residues on the surfaces of catalysts. These results are also demonstrated by the results of scanning electron micrography (SEM) and energy disperse spectrography (EDS).

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Keywords: Catalysis; Trichloroethylene; Zinc oxide; Sol–gel; FT-IR

1. Introduction

The widespread presence of chlorinated volatile organic compounds (VOCs) in the environment poses a serious environmental challenge because most of them are carcinogenic, toxic and extremely persistent in the environment. In this study, TCE is chosen as the probe contaminant because its emissions are associated to a wide range of industrial processes and its vapor is of great environmental concern, as it represents one of the most commonly detected pollutants in hazardous waste sites and landfills in many countries [1–4].

Heterogeneous catalytic oxidation has been demonstrated as an efficient abatement technology for the removal of VOCs [1–7]. The activity and performance of catalyst are influenced

by their chemical compositions and preparation method. Catalysts reported for destructive oxidation of chlorinated VOCs mostly consist of transition metal oxides (titanium, vanadium, manganese, ferric, nickel, copper and zinc) and noble metals (platinum, palladium and rhodium) on acidic supports [3,7,8]. Noble metals have better catalytic activities but they are expensive and easily poisoned by the acid gases (SO₂ and HCl) in the exhaust. On the other hand, the catalytic activities of transition metal oxides are lower but they are cheaper and have higher tolerances to the acid gases [5,9]. The supports of catalysts include alumina, silica, zeolite, activated carbon, molecular sieve and so on. Lu et al. [10] compared the activities of ZnO coated on different supports, the conversions of methylbenzene by ZnO/MCM-41 was higher than that by ZnO/α-Al₂O₃ at 383 °C, and also higher than that by ZnO/β-zeolite and ZnO/SiO₂ at 361 °C. Kim [11] also compared the activities of CuO coated on different supports and their performances followed the sequence of CuO/α-Al₂O₃ > CuO/TiO₂ (rutile) > CuO/TiO₂ (anatase) > CuO/SiO₂.

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The performances of catalysts are not only influenced by their chemical compositions but also influenced by the operation conditions such as operating temperature, space velocity, and the types and concentrations of air pollutants [9]. Higher operating temperature promotes the decomposition efficiency of organic pollutants, but over temperature ($>700\text{ }^{\circ}\text{C}$) may cause the catalyst sintered or volatilized. Takemoto et al. [12] found that the conversion of CH_2O by $\text{Cu-ZnO/Al}_2\text{O}_3$ catalyst was increased with the increase of operating temperature. Nearly 100% CH_2O was converted at $150\text{--}200\text{ }^{\circ}\text{C}$. Space velocity is the reciprocal of retention time of a pollutant flowing through the catalyst reactor. With small space velocity, the retention time of pollutant in the catalyst reactor is long and the conversions of VOCs are increased. The types and characteristics of pollutants also have significant influences on the performances of catalysts. Kim [11] used a $\text{Cu}/\alpha\text{-Al}_2\text{O}_3$ catalyst to study the decompositions of different volatile organic compounds. The removal efficiency of toluene was the highest, the next was xylene, and benzene was the lowest. In addition, the performance of catalyst was decreased as the concentrations of pollutants were increased. Although TCE can be completely decomposed into CO_2 and HCl with the aids of catalysts, but some undesirable toxic byproducts may be formed in the catalytic reactions [1]. Driessen et al. [2] addressed that phosgene, dichloroacetic acid (DCAA), monochloroacetic acid (MCAA), and dichloroacetylchloride (DCAC) can be formed in the catalytic decomposition of TCE.

ZnO is one of the photo catalysts with a similar band gap of TiO_2 , which has shown to be, in some cases, a more active catalyst. Even more importantly, ZnO possess the selectivity for complete mineralization of chlorinated waste [1]. Moreover, ZnO can be used as a support and coated with copper to serve as a Cu-Zn catalyst for the synthesis of methanol [10].

Most researches reported the application of semiconductor metal oxide ZnO for the photo catalysis of organic pollutants; however, less study investigates the catalytic incinerations of chlorinated VOCs with $\text{ZnO/Al}_2\text{O}_3$ catalyst. This study tries to prepare granular $\text{ZnO/Al}_2\text{O}_3$ catalyst by modified oil-drop sol-gel process incorporated with incipient wetness impregnation method and estimates its performance on the catalytic decomposition of TCE. The effects of different preparation and operation conditions are also investigated.

2. Experimental methods

2.1. Preparation of granular catalyst

The granular support $\gamma\text{-Al}_2\text{O}_3$ of catalyst was prepared by a modified oil-drop sol-gel process [13,14]. The starting material of $\gamma\text{-Al}_2\text{O}_3$ granules was high-concentration (1.8 M) boehmite sol (from SASOL). The 1.8 M boehmite sol was first mixed with a small amount of 1 M HNO_3 (the volume ratio of acid/sol was 1:5). The modified sol was stirred for 15 min at $70\text{ }^{\circ}\text{C}$ by a magnetic stirrer. A dramatic decrease of the pH of the sol by adding HNO_3 substantially accelerated the gelation process. After aging for half an hour at $60\text{--}70\text{ }^{\circ}\text{C}$, the pure 1.8 M boehmite sol became very viscous and it could not be stirred by the magnetic stirrer

even at the maximum power. The very viscous sol was then transferred to a dropper as the starting material for the granulation process.

The granulation process included the generation of sol droplets by the dropper, shaping, partially gelating the droplets into spherical wet-gel granules in a paraffin oil layer (color: white; density: 0.7864 g/cm^3 ; kinematic viscosity: 34.5 cs at $40\text{ }^{\circ}\text{C}$, from J.T. Baker) and consolidating the structure of the wet-gel granules in a 8 wt.% ammonia solution layer. The paraffin oil layer and ammonia solution layer were kept at room temperature. The interface between the oil and ammonia solution was slowly stirred to facilitate the transport of wet granules across the interface. After aging in the ammonia layer for at least 45 min, the spherical wet-gel granules (about 1–2 mm in diameter) were removed from the ammonia solution, carefully washed with water and alcohol sequentially, dried at $40\text{ }^{\circ}\text{C}$ for 48 h, and finally calcined in air at $450\text{ }^{\circ}\text{C}$ for 6 h.

The active metal ZnO was coated by incipient wetness impregnation method [9]. The volume of impregnation solution was estimated to equal to the volume of granular support. The precursors of zinc oxide were then weighed and mixed with distilled water to prepare the impregnation solution. The concentration of zinc in the catalyst was set at 1, 5 and 10%, respectively. The granular Al_2O_3 support was then put into the impregnation solution and stirred at room temperature for 8 h. After the incipient wetness impregnation process, the granular catalysts were dried at $120\text{ }^{\circ}\text{C}$ for 12 h and calcined in air at $550\text{ }^{\circ}\text{C}$ for 6 h. Two types of zinc oxide precursors were used in this study to compare the differences. The first one was commercial zinc oxide powder with the average particle diameter of 100 nm. The second one was zinc nitride which is very soluble and can transform to zinc oxide by thermal calcinations. For easy expression, the catalysts prepared from different zinc oxide precursors are named as $\text{ZnO/Al}_2\text{O}_3(\text{O})$ and $\text{ZnO/Al}_2\text{O}_3(\text{N})$, respectively hereafter. It has to state that the precursor $\text{Zn}(\text{NO}_3)_2$ for $\text{ZnO/Al}_2\text{O}_3(\text{N})$ catalyst can transform into ZnO completely after calcination in air at $550\text{ }^{\circ}\text{C}$ for 6 h. There is no Zn_3N_2 or $\text{Zn}(\text{NO}_3)_2$ in the catalyst and that can be proved from the analyses results that no N peak was found in SEM/EDS spectra and no Zn_3N_2 or $\text{Zn}(\text{NO}_3)_2$ peak was found in XRPD spectra.

2.2. Test of catalyst activity

A catalysis reaction system was set up to measure the activity of granular $\text{ZnO/Al}_2\text{O}_3$ catalyst. As shown in Fig. 1, the experimental equipments are composed of pure gas cylinders, mass flow meters, a generator of volatile TCE gas, a quartz reaction tube, an electric heater, and a programmable temperature controller. The on-line gas analyzers of Fourier transform infrared spectrograph (FT-IR, Perkin-Elmer: Spectrum One) and Gas chromatograph-flame ionization detector (GC-FID, Varian: CP-3800) were used to monitor the concentrations of reaction products in the effluent. The concentration and flow rate of volatile TCE gas were accurately controlled by mass flow meters. The total flow rate and concentration of TCE gas were controlled at 500 ml min^{-1} and 450 ppm, respectively. The flow rates of air and N_2 were controlled at 480 and 0 ml min^{-1} as the

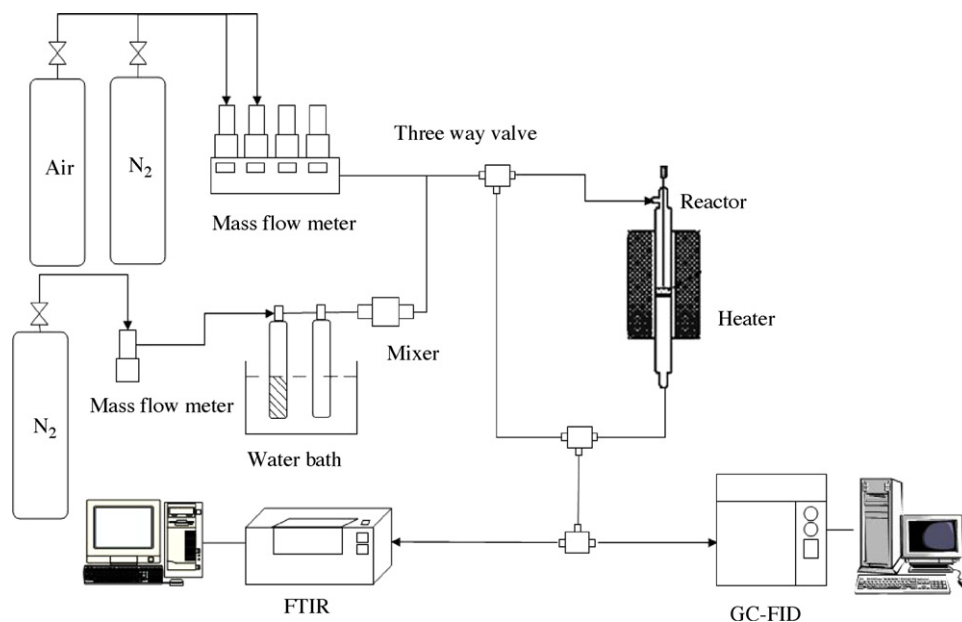


Fig. 1. Diagram of experimental apparatus.

influent O₂ concentration was 21%. The other 20 ml min⁻¹ N₂ was used to evaporate pure TCE liquid (from J.T. Baker) to generate TCE gas. The temperature of water bath in the generator of TCE gas was controlled at 40 °C. The concentration of generated TCE gas was rechecked by FT-IR gas analyzer and required to keep steady at least for 5 min before performing every test. After that, 0.67 g ZnO/Al₂O₃ catalysts were put in the middle of quartz tube and fixed from both sides by quartz fibers. As the reaction temperature was preheated to the required value and kept steady for 25 min, the generated TCE gas was introduced into the quartz tube and the gas analyzer FT-IR was turned on. The compositions and concentrations of reaction products in the effluent of catalyst reactor were continuously scanned and monitored. The scanning range of FT-IR spectra was 450–4000 cm⁻¹ and the instrument resolution was 4 cm⁻¹. The concentrations of TCE and other compounds were also analyzed and rechecked by GC-FID. The operation temperatures of GC-FID were 200 °C at injector, 180 °C at column (equity-5) and 200 °C at detector. To confirm the conversion of TCE was complete and stable, each test was performed for at least 50 min. After the catalyst test was finished, the flow meters and electric heater were shut down and the reacted catalyst was taken out for further analyses. Table 1 lists the experimental conditions of every test.

2.3. Characteristic analyses of catalyst

The surface areas of catalysts were measured at 77 K by the gravimetric methods with a vacuum microbalance (Micromeritics: Gemini 2360). These results provide a comparison of the surface area between fresh and reacted catalysts. N₂ adsorption–desorption procedure was used to determine the textural properties. The Brunauer–Emmett–Teller (BET) surface area was calculated from the adsorption isotherm. The average pore diameter was obtained from the pore size distribution. An X-ray powder diffractometer (XRPD, SIEMENS: D5000) with a Cu K α radiation was used to identify the crystalline species of zinc and aluminum on the catalyst. Diffraction patterns were manually analyzed with JCPDS card (standard patterns). The scanning range of 2θ was 20–80° in steps of 0.04°. The scanning speed was 4° min⁻¹. The surface structure and the accumulation of contaminants on the surface of reacted catalyst were observed by a scanning electron microscope (SEM, TOPCON: ABT-150S) at the Regional Instrument Center in National Chung-Hsing University (Taichung City, Taiwan). The acceleration voltage was 0.5–40 kV and the resolution was 4 nm. The samples used for SEM micrography needed drying for 8 h at 105 °C in an oven and stored in a desiccator

Table 1
List of experimental conditions

Run	Catalyst	Impregnation concentration of Zn (wt.%)	Calcinations temperature (°C)	Operation temperature (°C)	Oxygen concentration (%)	Space velocity (h ⁻¹)
1–5	–	–	–	30, 150, 250, 350, 450	21	36000
6–10	ZnO/Al ₂ O ₃ (N)	10	550	30, 150, 250, 350, 450	21	36000
11–15	ZnO/Al ₂ O ₃ (O)	10	550	30, 150, 250, 350, 450	21	36000
16–18	ZnO/Al ₂ O ₃ (N)	10	550	450	5, 10, 15	36000
19–21	ZnO/Al ₂ O ₃ (N)	10	550	450	21	12000, 18000, 72000
22–24	ZnO/Al ₂ O ₃ (N)	1, 5, 10	550	450	21	36000
25–27	ZnO/Al ₂ O ₃ (N)	10	450, 650, 750	450	21	36000

to prevent the interference of moisture. The compositions and relative amounts of elements on the surface of catalyst were determined by an energy dispersive spectroscopy (EDS, LINK: exLII) with a KeveX superdry detector. In addition, the prepared catalysts were also analyzed by the electron spectroscopy for chemical analysis system (ESCA, VG Scientific: ESCALAB 250) using Mg K α ($h\nu = 1253.6$ eV) as the radiation source to confirm their chemical compositions.

3. Results and discussions

3.1. Characteristics of granular ZnO/Al₂O₃ catalyst

The characteristics of granular ZnO/Al₂O₃ catalyst prepared by modified oil-drop sol–gel process and incipient wetness impregnation method was measured before the activity test. Table 2 indicates that the BET surface areas of fresh Al₂O₃ support, ZnO/Al₂O₃(O) and ZnO/Al₂O₃(N) catalysts are 386.8,

Table 2
BET surface area of ZnO/Al₂O₃ catalyst

Catalyst	BET surface area (m ² /g)
Al ₂ O ₃ (support)	386.8
ZnO/Al ₂ O ₃ (O) (fresh)	297.0
1% ZnO/Al ₂ O ₃ (N) (fresh)	209.3
5% ZnO/Al ₂ O ₃ (N) (fresh)	201.0
ZnO/Al ₂ O ₃ (N) (30 °C reacted)	368.0
ZnO/Al ₂ O ₃ (N) (150 °C reacted)	173.3
ZnO/Al ₂ O ₃ (N) (250 °C reacted)	187.5
ZnO/Al ₂ O ₃ (N) (350 °C reacted)	187.9
ZnO/Al ₂ O ₃ (N) (450 °C reacted)	171.3

297 and 209.3 m² g⁻¹, respectively. The surface area of fresh Al₂O₃ support is greater than that of general commercial support, but is decreased after the impregnation of active metal ZnO. The surface area of ZnO/Al₂O₃(O) catalyst is greater than that of ZnO/Al₂O₃(N), implying that using nano-ZnO powder as the precursor of active metal is better than Zn(NO₃)₂ for the preparation of ZnO/Al₂O₃ catalyst. This result can be illustrated by the SEM micrographs of fresh ZnO/Al₂O₃(N) and ZnO/Al₂O₃(O) catalysts (Fig. 2). The surface and pore distributions of fresh ZnO/Al₂O₃(N) catalyst are smooth and clogged, while the surface of fresh ZnO/Al₂O₃(O) catalyst is porous and uniform. Fig. 3 shows the EDS spectra of fresh Al₂O₃ support, ZnO/Al₂O₃(N) and ZnO/Al₂O₃(O) catalysts. The result illustrates that aluminum and zinc are the major elements in the ZnO/Al₂O₃(N) and ZnO/Al₂O₃(O) catalysts, and indicates that the catalysts are not contaminated with other elements during the preparation processes.

To confirm the chemical composition of active metals in the ZnO/Al₂O₃ catalyst, the electron spectroscopy spectra of granular catalysts are provided in Fig. 4. The binding energies of Zn 2p_{3/2}, Zn 2p_{1/2} and O 1s are 1019.9, 1042.70 and 530.5 eV, respectively. They are identical to the standard spectra of Zn²⁺ and O²⁻ [15–17]. ZnO is therefore proved to be the major active species in the catalyst. There is no peaks for N 1s (398.8 eV) and Zn₃N₂ observed in the XPS spectra of ZnO/Al₂O₃(N) catalyst, because the catalyst is prepared at low nitride concentrations (1, 5 and 10%) and the corresponding N concentrations are very low (0.34, 1.7 and 3.4%) and the catalyst is calcined in air at 550 °C for 6 h to completely convert the zinc nitride into zinc oxide. This can be proved from the analyses results that no N peak is found in SEM/EDS spectra and no Zn₃N₂ or Zn(NO₃)₂ peak

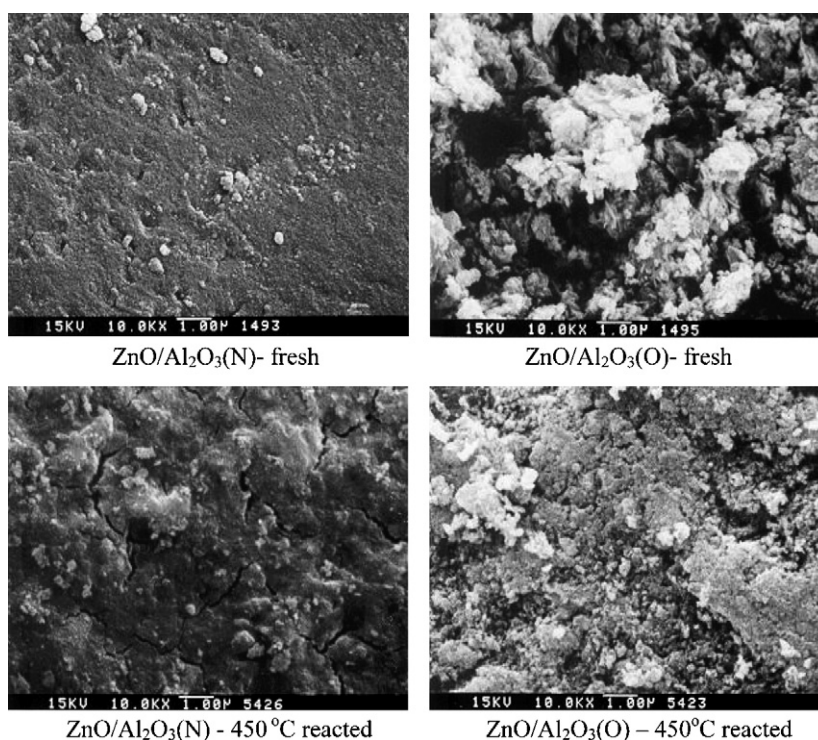


Fig. 2. SEM micrographs of ZnO/Al₂O₃(N) and ZnO/Al₂O₃(O) catalysts (fresh and reacted).

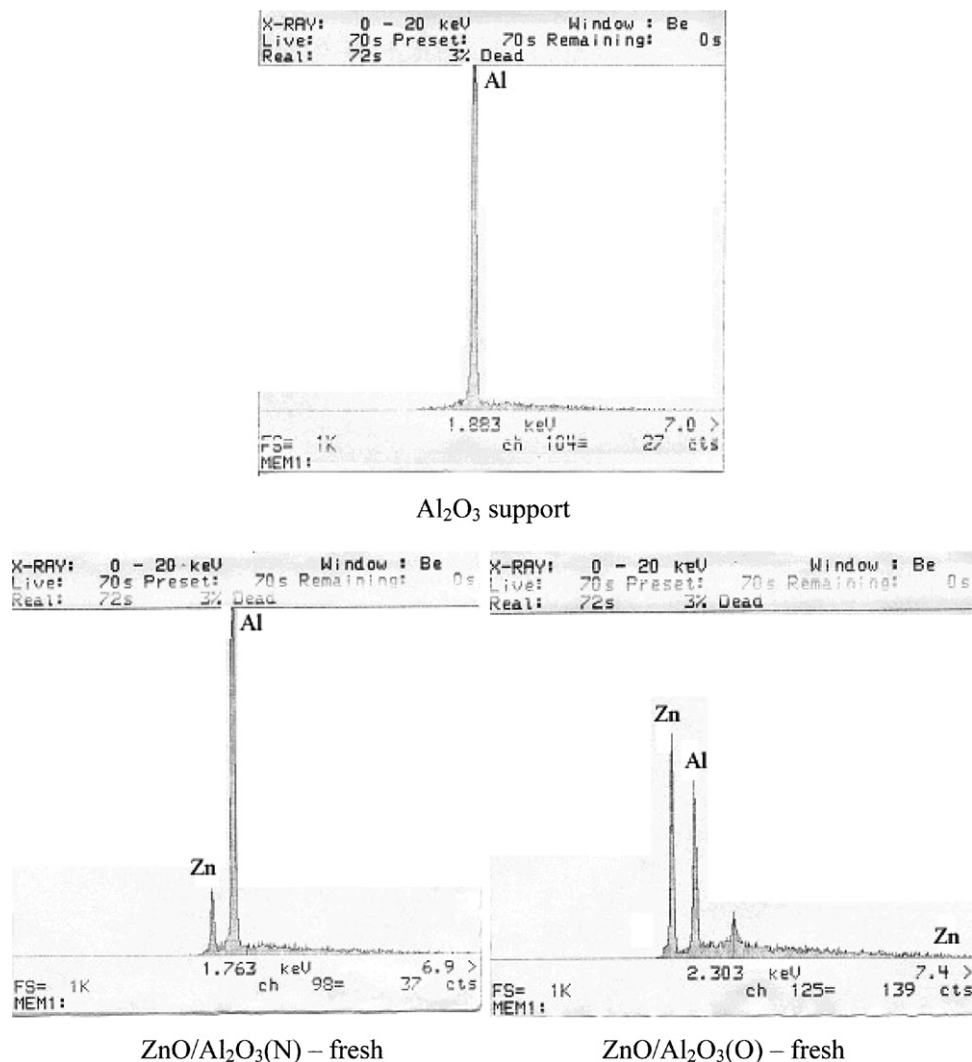


Fig. 3. EDS spectra of fresh Al_2O_3 support and $\text{ZnO}/\text{Al}_2\text{O}_3$ catalysts.

is found in XRPD spectra. On the other hand, the O 1s peak in the XPS spectra is smooth, symmetrical and locates at 530.5 eV for $\text{ZnO}/\text{Al}_2\text{O}_3(\text{O})$ and 531.0 eV for $\text{ZnO}/\text{Al}_2\text{O}_3(\text{N})$. The O 1s peak at 530.5 eV for $\text{ZnO}/\text{Al}_2\text{O}_3(\text{O})$ is attributed to Zn–O bonds because this value is in good agreement with previous references [16–18]. The O 1s peak at 531.0 eV for $\text{ZnO}/\text{Al}_2\text{O}_3(\text{N})$ shifts 0.5 eV toward higher binding energy side from the O 1s peak for Zn–O bonds. This shows that few O–H bonds may be formed due to absorbed H_2O molecules on the catalyst [18].

3.2. Effect of different catalyst preparation conditions

3.2.1. Different active metal precursors

Fig. 5 shows the conversions of TCE by different $\text{ZnO}/\text{Al}_2\text{O}_3(\text{N})$ and $\text{ZnO}/\text{Al}_2\text{O}_3(\text{O})$ catalysts at different operation temperature. The other operation conditions were identical: TCE 450 ppm, oxygen 21%, operation temperature 450 °C and space velocity $36,000\text{ h}^{-1}$. Without catalyst (blank test), the conversion of TCE is slightly increased with the increase of operation temperature and is only 13% at 450 °C. As the

$\text{ZnO}/\text{Al}_2\text{O}_3(\text{N})$ and $\text{ZnO}/\text{Al}_2\text{O}_3(\text{O})$ catalysts are present, the conversions of TCE are improved, especially at the operation temperature of 450 °C. The performance of $\text{ZnO}/\text{Al}_2\text{O}_3(\text{N})$ catalyst is slightly better than that of $\text{ZnO}/\text{Al}_2\text{O}_3(\text{O})$ as the operation temperature is higher than 250 °C. The best conversion of TCE by $\text{ZnO}/\text{Al}_2\text{O}_3(\text{N})$ catalyst is 94% at 450 °C. From the FT-IR spectra of reaction products (Fig. 6), the peaks of CO and HCl can be observed besides the major compound TCE. The peak of CO emitted from the catalytic incineration of TCE at 450 °C by $\text{ZnO}/\text{Al}_2\text{O}_3(\text{O})$ is higher than that by $\text{ZnO}/\text{Al}_2\text{O}_3(\text{N})$. Because CO is a major byproduct of incomplete oxidation of hydrocarbons, the higher concentration of CO means a lower catalytic activity. Therefore, both $\text{ZnO}/\text{Al}_2\text{O}_3(\text{N})$ and $\text{ZnO}/\text{Al}_2\text{O}_3(\text{O})$ catalysts have catalytic activities for TCE decomposition and $\text{ZnO}/\text{Al}_2\text{O}_3(\text{N})$ is better than $\text{ZnO}/\text{Al}_2\text{O}_3(\text{O})$.

3.2.2. Different concentrations of active metal

Fig. 7 shows the conversions of TCE by $\text{ZnO}/\text{Al}_2\text{O}_3(\text{N})$ catalyst with different concentrations of active metal (1, 5 and 10%).

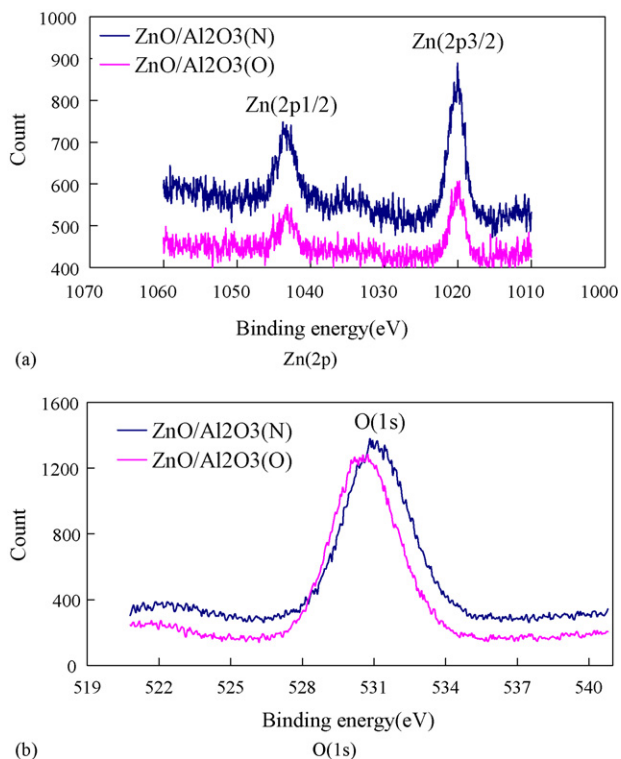


Fig. 4. ESCA spectra of ZnO/Al₂O₃(O) catalyst: (a) Zn 2p and (b) O 1s.

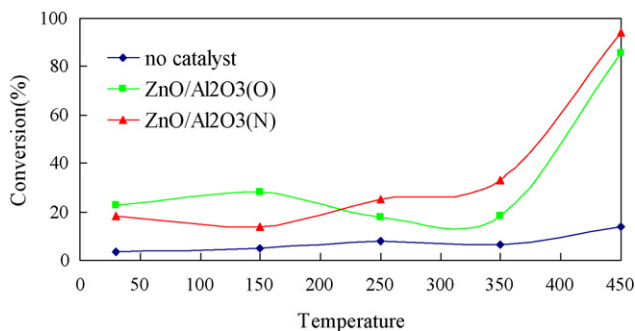


Fig. 5. Conversions of TCE by ZnO/Al₂O₃(O) catalysts at different operation temperatures.

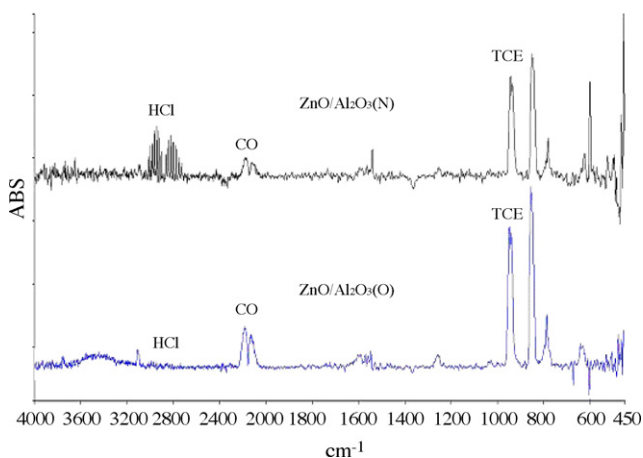


Fig. 6. FT-IR spectra for the effluent reaction products.

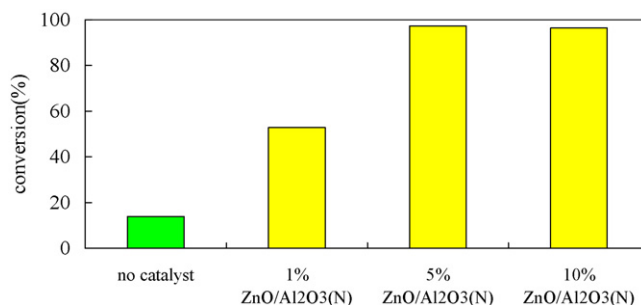


Fig. 7. Conversions of TCE by ZnO/Al₂O₃(N) catalysts with different concentrations of active metal.

The operation temperature and space velocity were all controlled at 450 °C and 36,000 h⁻¹, respectively. The conversions of TCE by granular catalysts coated with 5 and 10% active metal (ZnO) are similar and both are higher than 96%. The conversion of TCE by the catalyst coated with 1% ZnO is lower than 60%. More active metal coated on the support of catalyst is supposed to provide more reaction sites for catalytic decomposition of TCE gas. On the other hand, the BET surface areas of the ZnO/Al₂O₃(N) catalysts coated with 1, 5 and 10% ZnO are 209.3, 201 and 195.5 m² g⁻¹, respectively. The BET surface area of catalyst is slightly decreased as the concentration of active metal increased. Catalyst coated with too much active metal will block its surface area and is more expensive. Therefore, the granular catalyst coated with 5% active metal is considered to be the effective and economic one in our experiment.

3.2.3. Different calcination temperatures

Fig. 8 shows the conversions of TCE by ZnO/Al₂O₃(N) catalyst prepared at different calcination temperatures (450, 550, 650 and 750 °C). The other operation conditions are identical. ZnO/Al₂O₃(N) catalyst prepared at the calcination temperature of 550 °C has better performance. Calcination temperature can influence the characteristic of active metal, and the porosity and surface areas of catalysts [10,13,14,17]. This result can also be illustrated by the SEM micrographs in Fig. 9. The surface morphology of ZnO/Al₂O₃(N) catalyst calcined at 550 °C has more and uniform porosity than that at 450 and 650 °C. Moreover, the surface of ZnO/Al₂O₃(N) catalyst is sintered and melted at higher calcination temperatures 650 and 750 °C.

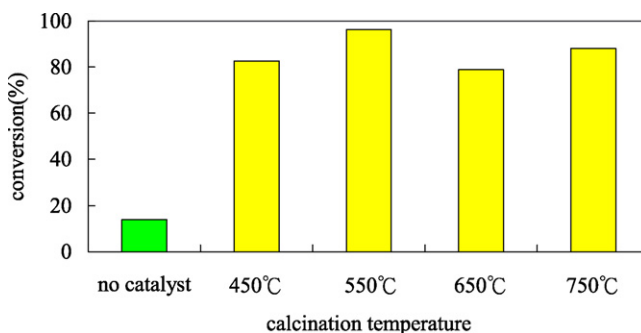


Fig. 8. Conversions of TCE by ZnO/Al₂O₃(N) catalysts prepared at different calcination temperatures.

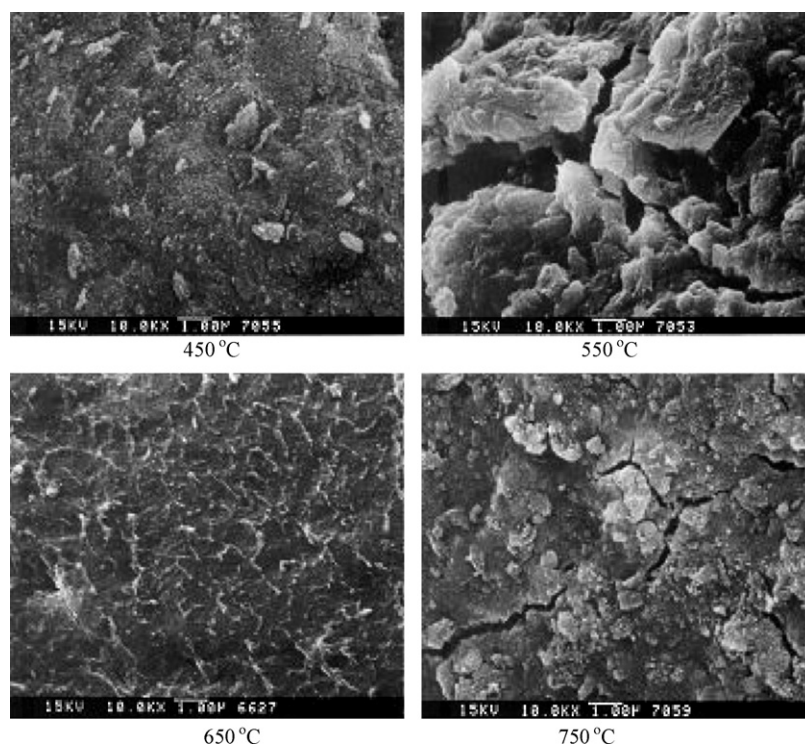


Fig. 9. SEM micrographs of ZnO/Al₂O₃(N) catalysts prepared at different calcinations temperatures.

3.3. Effect of different catalytic reaction conditions

3.3.1. Different reaction temperatures

Fig. 10 shows the conversions of TCE by ZnO/Al₂O₃(N) catalyst at different reaction temperatures. The conversion of TCE is increased from 18 to 33% as the reaction temperature is increased from 30 to 350 °C. A significant increase of TCE conversion (94%) can be observed as the reaction temperature rises to 450 °C. As a result, the performance of ZnO/Al₂O₃(N) catalyst is outstanding at high operation temperature 450 °C. This finding is also identical to the studies of Liu et al. [19] and Takemoto et al. [12]; both indicated that the activities of catalysts for the decomposition of organic pollutants were increased with the temperature.

From the EDS analyses, some peaks of elemental chlorine can be found on the reacted ZnO/Al₂O₃(N) catalyst as the oper-

ation temperature was higher than 250 °C, which demonstrated that TCE is significantly decomposed by the ZnO/Al₂O₃(N) catalyst at such temperature. Moreover, the BET surface area of ZnO/Al₂O₃(N) catalyst is reduced to 170–185 m² g⁻¹ as the reaction temperatures were higher than 150 °C (Table 2). The decreases of BET surface areas at high temperatures are attributed to the sintering of catalyst materials and the aggregations of reaction residues on the surface of catalysts. The surface morphologies of fresh and reacted catalysts are quite different. As shown in Fig. 3, the surface and porosity of fresh catalyst are smooth and uniform, while the reacted catalysts are sintered, melted, or blocked with reaction residues. These phenomena are especially evident for the reacted catalysts which operation temperature was 450 °C.

3.3.2. Different oxygen concentrations

For studying the effects of different oxygen concentrations on the performances of ZnO/Al₂O₃(N), the concentrations of oxygen in the feed gas were controlled at 21, 15, 10 and 5%, respectively. As shown in Fig. 11, the conversions of TCE by ZnO/Al₂O₃(N) catalyst are all higher than 95% at these four O₂ concentrations. This result indicates that the decomposition of TCE gas by ZnO/Al₂O₃(N) catalyst is not sensitive to these four O₂ concentrations, because these O₂ concentrations in the feed gas are much greater than the stoichiometric O₂ concentration (1913 ppm) required for the complete decomposition of TCE. This good performance of ZnO/Al₂O₃(N) catalyst at low O₂ concentration also provides a outstanding advantage in future application.

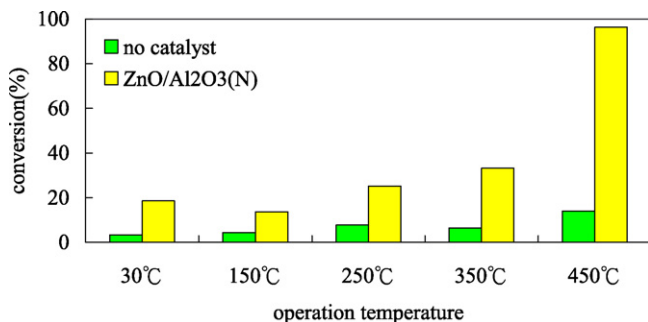


Fig. 10. Conversions of TCE by ZnO/Al₂O₃(N) catalysts at different operation temperatures.

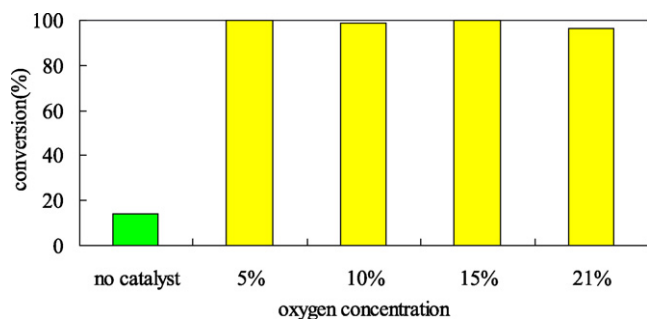


Fig. 11. Conversions of TCE by ZnO/Al₂O₃(N) catalyst at different oxygen concentrations.

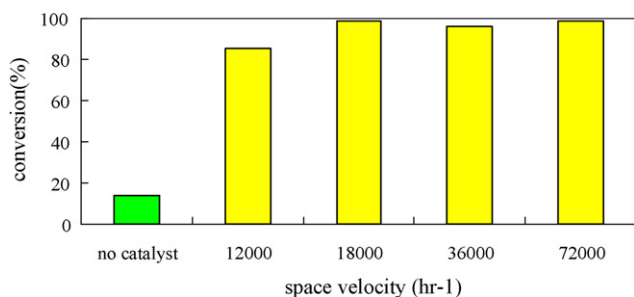


Fig. 12. Conversions of TCE by ZnO/Al₂O₃(N) catalysts at different space velocities.

3.3.3. Different space velocities

The conversions of TCE at different space velocities (72,000, 36,000, 18,000 and 12,000 h⁻¹) are shown in Fig. 12. The best conversion of TCE (98%) is occurred at space velocity 18,000 h⁻¹, the next is 72,000 h⁻¹ (97%), 36,000 h⁻¹ (96%), and the last is 12,000 h⁻¹ (85%). Decreasing space velocity increases the retention time of TCE gas in the catalyst bed and the conversion of TCE increases, but our results show that the conversion of TCE at space velocity 12,000 h⁻¹ is the least. This phenomenon can be interpreted from the FT-IR spectra of reaction products. As shown in Fig. 13, the peak intensities of CO and HCl become higher and lower, respectively, as the space

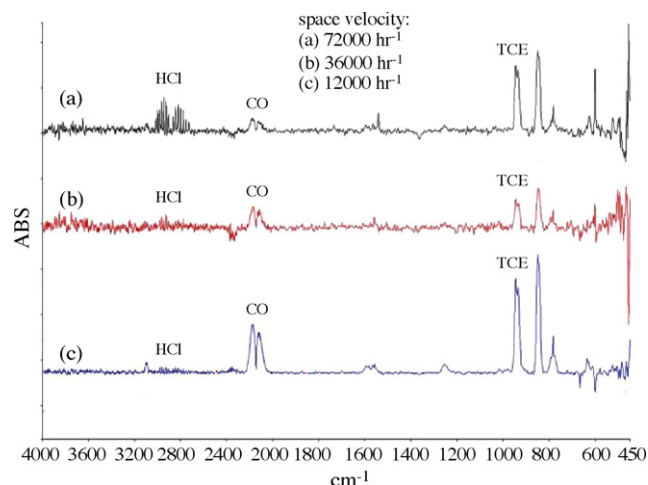


Fig. 13. FT-IR spectra for the effluent reaction products at different space velocities.

velocities are decreased from 72,000 to 12,000 h⁻¹. The higher concentrations of CO in the effluent gas indicate that the catalytic decomposition of TCE is not complete. Some residues are accumulated on the surface of catalyst and the performance of catalyst decreases.

4. Conclusion

This study tries to prepare granular ZnO/Al₂O₃ catalysts for the catalytic incineration of hazardous TCE gas. The effects of different preparation and operation conditions on the performances of catalysts are also investigated. Experimental results show that the granular ZnO/Al₂O₃ catalyst has good catalytic activities on TCE decomposition and the conversion of TCE is 98%. ZnO/Al₂O₃(N) catalyst has better performance than ZnO/Al₂O₃(O) at high operation temperature. Five percent of active metal concentration and 550 °C calcination temperature are the better and economic preparation conditions, and the optimum operation temperature and space velocity are 450 °C and 18,000 h⁻¹, respectively. The conversions of TCE are similar and all higher than 90% at these four O₂ concentrations in the feed gas. By FT-IR measurement, the major reaction products during catalytic decomposition of TCE are HCl and CO₂. The BET surface areas of catalysts are significantly decreased as the calcinations temperature is higher than 550 °C due to the sintering of catalyst materials and as the reaction temperature is higher than 150 °C due to the accumulations of reaction residues on the surfaces of catalysts. These results are also demonstrated by SEM micrographs and EDS spectra.

References

- [1] P.B. Amama, K. Itoh, M. Murabayashi, Photocatalytic oxidation of trichloroethylene in humidified atmosphere, *J. Mol. Catal. A* 176 (2001) 165–172.
- [2] M.D. Driessen, T.M. Miller, V.H. Grassian, Photocatalytic oxidation of trichloroethylene on zinc oxide: characterization of surface-bound and gas-phase products and intermediates with FT-IR spectroscopy, *J. Mol. Catal. A* 131 (1998) 149–156.
- [3] J.R. Gonz lez-Velasco, A. Aranzabal, J.I. Guti rrez-Ortiz, R. Lo pez-Fonseca, M.A. Guti rrez-Ortiz, Activity and product distribution of alumina supported platinum and palladium catalysts in the gas-phase oxidative decomposition of chlorinated hydrocarbons, *Appl. Catal. B* 19 (1998) 189–197.
- [4] S. Kawi, M. Te, MCM-48 supported chromium catalyst for trichloroethylene oxidation, *Catal. Today* 44 (1998) 101–109.
- [5] P.B. Amama, K. Itoh, M. Murabayashi, Gas-phase photocatalytic degradation of trichloroethylene on pretreated TiO₂, *Appl. Catal. B* 37 (2002) 321–330.
- [6] G.A. Atwooda, H.L. Greena, P. Chintawarb, R. Rachapudib, B. Ramachandranb, C.A. Vogelc, Trichloroethylene sorption and oxidation using a dual function sorbent/catalyst in a falling furnace reactor, *Appl. Catal. B* 18 (1998) 51–61.
- [7] M.M.R. Feijen-Jeurissen, J.J. Jorna, B.E. Nieuwenhuys, G. Sinquin, C. Petit, J.P. Hindermann, Mechanism of catalytic destruction of 1,2-dichloroethane and trichloroethylene over α-Al₂O₃ and α-Al₂O₃ supported chromium and palladium catalysts, *Catal. Today* 54 (1999) 65–79.
- [8] C. Lahousse, A. Bernier, P. Grange, B. Delmon, P. Papaefthimiou, T. Ioannides, X. Verykios, Evaluation of α-Al₂O₃–MnO₂ as a VOC removal catalyst: comparison with a noble metal catalyst, *J. Catal.* 178 (1998) 214–225.

- [9] J.C. Chen, M.Y. Wey, C.L. Yeh, Y.S. Liang, Simultaneous treatment of organic compounds, CO and NO_x in the incineration flue gas by three-way catalyst, *Appl. Catal. B* 48 (2004) 25–35.
- [10] W. Lu, G.Z. Lu, Y. Luo, A. Chen, A novel preparation method of ZnO/MCM-41 for hydrogenation of methyl benzoate, *J. Mol. Catal. A* 188 (2002) 225–231.
- [11] S.C. Kim, The catalytic oxidation of aromatic hydrocarbons over supported metal oxide, *J. Hazard. Mater.* 91 (2002) 285–299.
- [12] T. Takemoto, D. He, Y. Teng, A. Nakayama, K. Tabata, E. Suzuki, Enhancement of methanol selectivity in the products of direct selective oxidation of methane in CH₄–O₂–NO with Cu–ZnO/Al₂O₃, *J. Catal.* 198 (2001) 109–115.
- [13] Z.M. Wang, Y.S. Lin, Sol–gel synthesis of pure and copper oxide coated mesoporous alumina granular particles, *J. Catal.* 174 (1998) 43–51.
- [14] G. Buelna, Y.S. Lin, Preparation of spherical alumina and copper oxide coated alumina sorbents by improved sol–gel granulation process, *Micropor. Mesopor. Mater.* 42 (2001) 67–76.
- [15] C.D. Wagner, W.M. Riggs, J.F. Moulder, G.E. Muilenberg, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, Physical Electronic Division, USA, 1979, p. 321.
- [16] L. Jing, B. Wang, B. X. S. Li, K. Shi, W. Cai, H. Fu, Investigations on the surface modification of ZnO nanoparticle photocatalyst by depositing Pd, *J. Solid State Chem.* 177 (2004) 4221–4227.
- [17] Y. Liu, Z. Liu, G. Wang, Synthesis and characterization of ZnO nanorods, *J. Cryst. Growth* 252 (2003) 213–218.
- [18] M. Futsuhara, K. Yoshioka, O. Takai, Optical properties of zinc oxynitride thin films, *Thin Solid Films* 317 (1998) 322–325.
- [19] Y. Liu, Z. Wei, Z. Feng, M. Luo, P. Ying, C. Li, Oxidative destruction of chlorobenzene and *o*-dichlorobenzene on a highly active catalyst: MnO_x/TiO₂–Al₂O₃, *J. Catal.* 202 (2001) 200–204.