Elimination of formaldehyde over Cu-Al₂O₃ catalyst at room temperature

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Abstract: Catalytic elimination of formaldehyde (HCHO) was investigated over Cu-Al₂O₃ catalyst at room temperature. The results indicated that no oxidation of HCHO into CO_2 occurs at room temperature, but the adsorption of HCHO occurs on the catalyst surface. With the increase of gas hourly space velocity (GHSV) and inlet HCHO concentration, the time to reach saturation was shortened proportionally. The results of the *in situ* DRIFTS, Density functional theory calculations and temperature programmed desorption (TPD) showed that HCHO was completely oxidized into HCOOH over Cu-Al₂O₃ at room temperature. With increasing the temperature in a flow of helium, HCOOH was completely decomposed into CO_2 over the catalyst surface, and the deactivated Cu-Al₂O₃ is regenerated at the same time. In addition, although Cu had no obvious influence on the adsorption of HCHO on Al₂O₃, Cu dramatically lowered the decomposition temperature of HCOOH into CO_2. It was shown that Cu-Al₂O₃ catalyst had a good ability for the removal of HCHO, and appeared to be promising for its application in destroying HCHO at room temperature.

Keywords: formaldehyde; Cu-Al₂O₃; *in situ* DRIFTS; TPD

Introduction

Formaldehyde (HCHO), which is emitted from building and furnishing materials and consumer products, is the dominating volatile organic compound (VOC) in the indoor environment (Yu, 1998). In addition, formaldehyde is known to cause nasal tumors, irritation of the mucous membranes of the eyes and respiratory tract, and skin irritation (Collins, 2001). Due to the increasing concern about its emission, the abatement of its emission at lower temperature is of significant practical interest.

Catalytic oxidation is an effective way to control emission of VOCs because VOCs can be oxidized into CO_2 over catalysts at much lower temperatures than those of thermal oxidation (Spivey, 1987; Sciré, 2003; 2001). However, it is still very difficult for the method of catalytic oxidation to eliminate HCHO at room temperature. The removal of HCHO by using adsorbents has also been studied both in the lab and in the field (Eriksson, 1980; Arthur, 1981; Sekine, 2001). Eriksson *et al.* (Eriksson, 1980) have attempted to remove gaseous HCHO using potassium permanganate, activated carbon and aluminum oxide and so on. Arthur (Arthur, 1981) tested filter beds of potassium permanganate in a mobile house with active airflow. The HCHO concentration was dropped from 1.3—1.8 to 0.2—0.3 ppm within a few hours but returned to its initial level after 1—5 d. Recently, Sekine *et al.* (Sekine, 2001) have developed a board-like air-cleaning material consisting of activated carbon particles and manganese oxides. They have found that the material not only reduced indoor HCHO concentration from 0.21 to 0.04 ppm for more than 7 months, but also enhanced the loss of HCHO gas from building material in apartments.

Using adsorbents can effectively remove the HCHO at room temperature, but the adsorbents were deactivated after a period. Up to now, neither the work on the mechanism of deactivation nor the study on the regeneration of the deactivated material has been discussed in detail.

Sekine *et al.* (Sekine, 2001) have reported that some transition metal oxides could react with HCHO at room temperature, copper oxides showed the highest reactivity with HCHO. The aim of the present work is to investigate the removal of HCHO on Cu supported alumina catalyst at room temperature. In addition, the characterization of Cu-Al₂O₃

was carried out by *in situ* DRIFT, Density functional theory calculations and TPD. The mechanism of deactivation and regeneration of the deactivated Cu-Al₂O₃ were also discussed on the basis of the experimental results.

1 Experimental

1.1 Catalyst preparation

Utilized Al₂O₃ (gamma type) has a total BET surface area of 250 m^2/g as supportor Cu-Al₂O₃ 10 wt.% catalyst, was prepared by an impregnation method with an aqueous solution of copper nitrate, followed by evaporation to dryness in a rotary evaporator under a reduced pressure at 333 K. The wet sample obtained was dried at 393 K for 12 h, then calcined in air at 873 K for 3 h. Before the catalytic tests, the catalysts were sieved into 40—60 meshes.

1.2 Activity tests

The activity tests for the catalytic oxidation of HCHO over Cu-Al₂O₃ catalyst were performed with a fixed-bed quartz flow reactor by passing a gas mixture of HCHO/O₂/He = 300 ppm/20 vol%/balance at a flow rate of 50 cm^3/min (GHSV: 10000, 30000, 50000 h^{-1} by changing the catalyst volume) at room temperature. HCHO standard gas was constantly introduced from a gas-generator system (Sekine, 2001). HCHO, CO and CO_2 were analyzed using a gas chromatograph (GC) equipped with hydrogen flame ionization detector (FID). In addition, the effluent gas was monitored by an on-line quadrupole mass spectrometer (Aglient, 5973N).

1.3 DRIFTS

DRIFT and *in situ* DRIFT spectra were recorded in a NEXUS 670-FTIR equipped with a smart collector and a liquid N₂ cooled MCT detector. The sample (about 30 mg) for study was finely grounded and placed in a ceramic crucible. A flow of feed gas mixture was controlled by mass flow meters. All spectra were measured with a resolution of 4 cm^{-1} and accumulating 100 scans. A background spectrum was subtracted from each spectrum, respectively.

1.4 Density functional theory calculations

All calculations were performed by a Gaussian 98 program package with a Cerius 2 interface. Becke's three-parameter hybrid functional using the correlation functional of Lee, Yang and Parr (B3LYP) was used with a 3-21G basis

set. The calculated vibration frequencies and infrared intensity of the vibrational normal modes were picked up by the Hyperchem™ Version 6.0 package.

1.5 TPD

Temperature programmed desorption (TPD) test was performed in a quartz U-shape reactor in a flow of 40 cm^3/ min helium with a constant heating rate of 20 K/min. The TPD was recorded by an Agilent quadrupole mass spectrometer(5973 N) at the temperature range of 298—773 K. Before the experiments, sample was pretreated at room temperature in the case of catalytic activity test.

2 Results and discussion

2.1 Elimination of HCHO

Fig.1 illustrates the HCHO conversions as a function of time over Cu-Al$_2$O$_3$ catalyst where the GHSV varied at 10000 h^{-1}, 30000 h^{-1} and 50000 h^{-1} at room temperature in a flow gas of HCHO(300 ppm), oxygen(20 vol %) and balance gas helium. It could be seen that the HCHO conversions were almost 100% at the beginning of the reaction, and then slowly dropped to zero over Cu-Al$_2$O$_3$. With increase of the GHSV from 10000 h^{-1} to 30000 h^{-1} and 50000 h^{-1}, the times for the conversion to decrease to zero were shortened from about 2100 to 700 and 400 min, respectively.
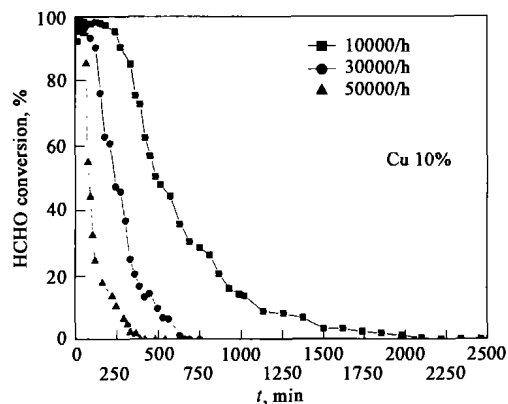

Fig.1 Time courses of formaldehyde(HCHO) conversions over Cu-Al$_2$O$_3$ at room temperature with inlet HCHO concentration of 300 ppm and different GHSV: 10000, 30000, 50000 h^{-1}

Fig.2 shows the profiles of the time courses of HCHO conversion over Cu-Al$_2$O$_3$ at room temperature on a fixed GHSV of 50000 h^{-1} and with different inlet HCHO concentrations of 200, 300 ppm. The profiles of HCHO conversions were very similar to that shown in Fig.1. The time to reach zero conversion was apparently shortened from 650 min to 400 min with increasing inlet HCHO concentration from 200 ppm to 300 ppm. In addition, it was noteworthy that CO and CO$_2$ were not detected in effluent gases during the removal of HCHO at all of the above conditions.

Fig.3 shows the time courses of HCHO conversions over Cu-Al$_2$O$_3$ and Al$_2$O$_3$ at room temperature with 300 ppm inlet HCHO concentration at the GHSV of 50000 h^{-1}. The profile of HCHO conversions and the time to reach zero conversion over Al$_2$O$_3$ are almost the same as those over Cu-Al$_2$O$_3$. It showed that Cu has no an obvious promoting effect to Al$_2$O$_3$ for reducing HCHO concentration. Eric *et al*.(Cordi, 1997) have reported that the same amount of VOCs could be adsorbed on Cu-Al$_2$O$_3$ catalyst and Cu-free alumina because alumina has a much higher surface area than Cu, which could
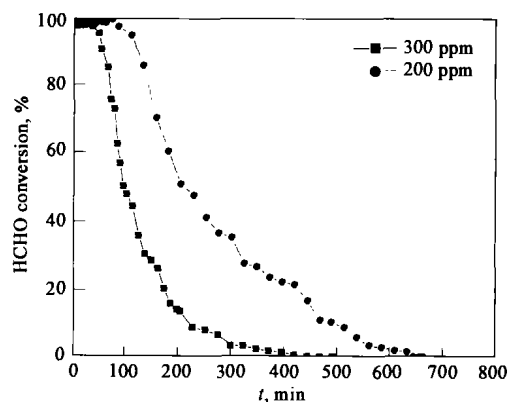

Fig.2 Time courses of formaldehyde(HCHO) conversions over Cu-Al$_2$O$_3$ at room temperature with different HCHO concentrations and the GHSV of 50000h^{-1}

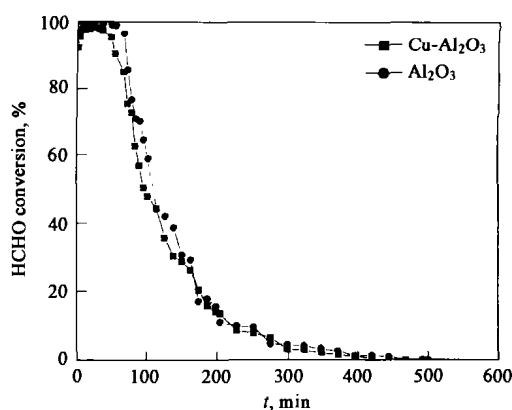be a reasonable explanation for our results.

Fig.3 Time courses of formaldehyde(HCHO) conversions over Cu-Al$_2$O$_3$ and Al$_2$O$_3$ at room temperature with 300 ppm HCHO and the GHSV of 50000 h^{-1}

The above results indicated that at room temperature, the adsorption of HCHO occurred on the catalyst surface instead of the oxidation of HCHO into CO$_2$, and the changes of the HCHO conversions were due to the different adsorption over the Cu-Al$_2$O$_3$ at various GHSVs and inlet HCHO concentrations. Once the adsorption on the catalyst surface reached saturation, the HCHO conversion would decrease to zero, simultaneously the Cu-Al$_2$O$_3$ was deactivated. In addition, with increasing GHSV and inlet HCHO concentration, the time to reach saturation was proportionally shortened. It could be concluded that the Cu-Al$_2$O$_3$ could keep its ability longer for the elimination of HCHO under the conditions of lower GHSV and HCHO concentration.

2.2 DRIFTS and Density functional theory calculations

Fig.4 shows the comparison of DRIFT spectra collected on the fresh Cu-Al$_2$O$_3$ and the used Cu-Al$_2$O$_3$. Bands at 2897, 2856, 2807, 2704 1597, 1392, 1379, 1352 cm^{-1} were observed on the catalyst surface. Fig.5 shows the *in situ* DRIFT spectra of Cu-Al$_2$O$_3$ catalyst in a flow of N$_2$ at various temperatures (303—553 K) after HCHO + O$_2$ adsorption for 600 min on the Cu-Al$_2$O$_3$. The appeared bands were in agreement with those of Fig.4. According to previous studies, two strong bands at 1597 and 1352 cm^{-1} were ascribed to v_{as} (COO) and v_s (COO) (Boccuzzi, 2003; Millar, 1995; Liu, 2003; Popova, 2000), the small and shoulder bands at 2897, 2856, 2807, 2704 cm^{-1} were

assigned to υ (C—H) (Millar, 1995; Liu, 2003; Popova, 2000), and the peaks at 1392, 1379 cm⁻¹ were assigned to δ (C—H) (Millar, 1995; Liu, 2003; Popova, 2000). No peak of the adsorbed HCHO could be observed, even at room temperature. The findings showed that a large amount of HCOOH was formed over Cu-Al₂O₃ surface.
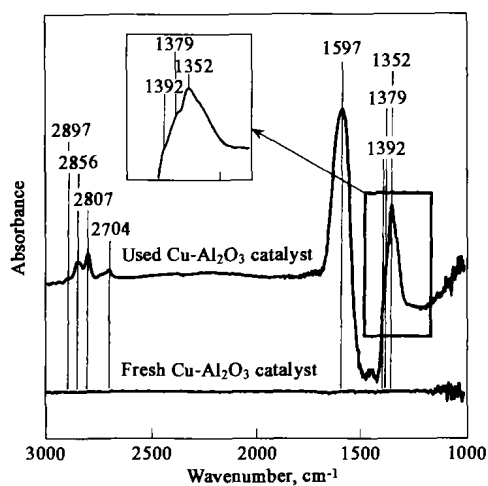

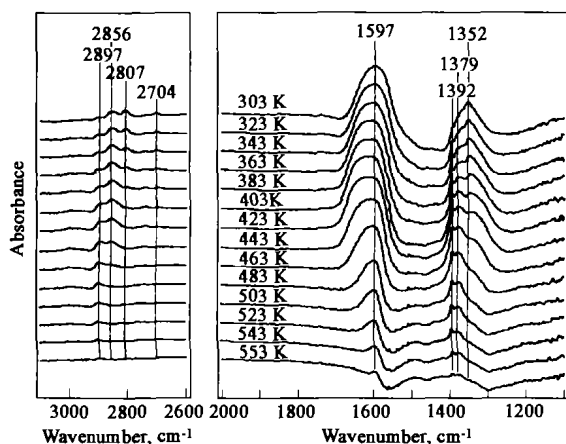Fig.4   Comparison of DRIFT spectra on the fresh and the used Cu-Al₂O₃ catalysts

Fig.5   *In situ* DRIFT spectra of Cu-Al₂O₃ catalyst in a flow of N₂ mixture at various temperatures(303—553 K) after HCHO + O₂ adsorption for 600 min on the Cu-Al₂O₃ catalyst

The calculation model and optimized structure for the absorbed HCOOH on Cu-Al₂O₃ were shown in Fig. 6, respectively. The optimized distance between the oxygen atom in HCOO⁻ and the aluminum atom in Cu-Al cluster was 1.96×10^{-10} m.
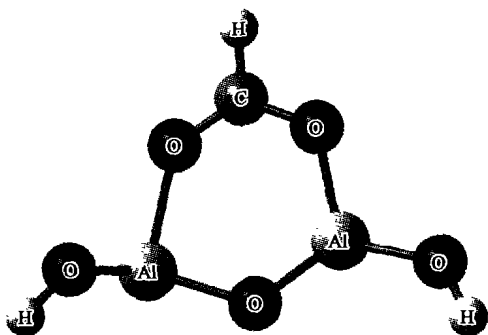

Fig.6   Optimized structure of the computational model for formate species on Al₂O₃ catalyst

As shown in Fig.7, the calculated FTIR spectrum was of reasonable similarity to the corresponding experimental one

(Fig. 4 and Fig. 5). The asymmetric stretching vibration mode of the formate species on Cu-Al₂O₃ catalyst was calculated at 1582 cm⁻¹ with 309 km/mol intensity, which was very close to the experimental value of 1586 cm⁻¹ with high absorbance. The calculated symmetric stretching vibrational mode of the formate species on Cu-Al₂O₃ (1299 cm⁻¹) was 53 cm⁻¹ lower than the experimental value of 1352 cm⁻¹. Through the analysis of the vibration mode and the vibration frequency, we concluded that there is an excellent agreement between the calculational vibration spectrum and the experimental one.
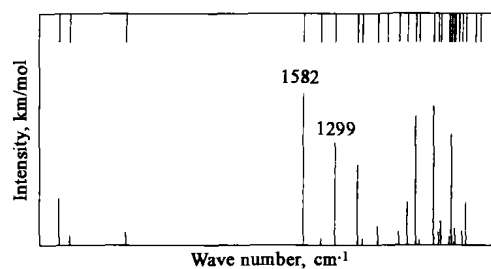

Fig.7   Calculated vibrational IR spectra for the computational model at B3LYP/3-21G level

2.3   TPD

Fig.8 shows the TPD patterns of CO₂ on the 10 wt.% Cu-Al₂O₃ and Al₂O₃ after exposing the catalyst to HCHO + O₂ mixture for 600 min at room temperature, followed by heating the sample to 773 K in a flow of 40 cm³/min helium. The main product of HCOOH decomposition on the Cu-Al₂O₃ and Al₂O₃ was CO₂ (m/z = 44) over a broad temperature range(298—773 K). The profile of the desorbed CO₂ showed that HCOOH decomposition on Cu-Al₂O₃ started even at 300 K, then reached highest intensity at about 423 K, and the decomposition temperature was much lower than that on Al₂O₃ (~ 573 K). Fig.8 also shows that the amount of CO₂ desorbed from Cu-Al₂O₃ was almost the same as that from Al₂O₃, which was in good accordance with the results shown in Fig.3. In addition, no by-product was detected over the entire temperature range examined.
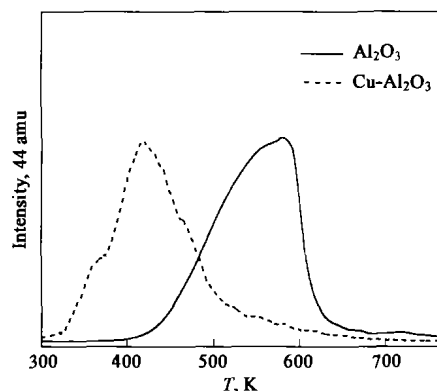

Fig.8   CO₂ TPD patterns of Cu-Al₂O₃ and Al₂O₃ after exposing them to HCHO + O₂ mixture for 600 min at room temperature

On the basis of the results above, we concluded that HCHO was completely oxidized into HCOOH on Cu-Al₂O₃ catalyst. With increasing the temperature, HCOOH was completely decomposed and oxidized into CO₂ over the catalyst surface. In addition, it was noteworthy that Cu

dramatically decease the temperature for HCOOH decomposition into CO_2 although that Cu had no obvious influence on the adsorption of HCHO on Al_2O_3 .

2.4 Regeneration

Fig. 9 showed the comparison of the time courses of HCHO conversion on a fixed GHSV of 50000 h^{-1} and with HCHO concentration of 300 ppm over fresh and regenerated $Cu-Al_2O_3$ at room temperature. Firstly, HCHO adsorption was performed over fresh $Cu-Al_2O_3$. After saturation, HCHO and O_2 were switched off, and $Cu-Al_2O_3$ was heated to 473 K in a flow of 40 cm^3/min helium. When the regenerated $Cu-Al_2O_3$ was cooled to room temperature, HCHO was passed through it again. The process was repeated twice. As shown in Fig.9, the profiles of HCHO conversions and the times to reach saturation over the regenerated $Cu-Al_2O_3$ are almost the same as that over the fresh $Cu-Al_2O_3$. These results indicated that the regenerated $Cu-Al_2O_3$ has a very similar ability for HCHO adsorption over the fresh $Cu-Al_2O_3$; furthermore, heating catalyst in oxidation atmosphere was an effective method for regeneration of the deactivated $Cu-Al_2O_3$ catalyst.
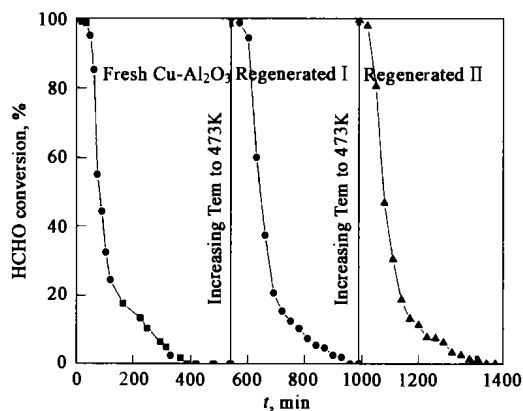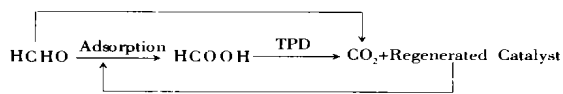

Fig.9 Comparison of the time courses of HCHO conversion on a fixed GHSV of 50000 h^{-1} and with inlet HCHO concentration of 300 ppm over fresh and refreshed $Cu-Al_2O_3$ at room temperature

2.5 Reaction scheme of HCHO oxidation

Scheme 1

On the basis of the obtained results, we propose Scheme 1 for the process of the HCHO elimination over $Cu-Al_2O_3$. HCHO firstly adsorbed on $Cu-Al_2O_3$ catalyst surface, and then was oxidized into HCOOH at room temperature. When the catalyst was exposed to HCHO + O_2 mixture for 600 min, the deactivated $Cu-Al_2O_3$ catalyst was heated to 773 K in a flow of 40 cm^3/min helium. HCOOH desorbed and decomposed to CO_2 completely, and the deactivated $Cu-Al_2O_3$ catalyst was regenerated and reused. In addition, HCHO could directly react with oxygen in the gas phase to be oxidized into CO_2 . However, it was well known that the gas phase reaction between HCHO and O_2 occurs at a much higher temperature, so the reaction could be ignored at room temperature. From the results obtained, we suggested that the HCHO was adsorbed by forming HCOOH at room temperature, but it completely decomposed into CO_2 by increasing temperature.

3 Conclusions

$Cu-Al_2O_3$ catalyst showed a good ability for the catalytic elimination of HCHO, and appeared to be promising for its application in destroying HCHO at room temperature. With increasing gas hourly space velocity(GHSV) and inlet HCHO concentration, the time to reach saturation was shortened proportionally. The results of the DRIFTS, Density functional theory calculations and TPD show that HCHO was completely oxidized into HCOOH over $Cu-Al_2O_3$ at room temperature. With increasing the temperature in a flow of helium, HCOOH was completely decomposed and oxidized into CO_2 over the catalyst surface, and the deactivated $Cu-Al_2O_3$ is regenerated at the same time. In addition, although Cu had no obvious influence on the adsorption of HCHO on Al_2O_3 , Cu dramatically decreased the temperature for HCOOH desorption into CO_2 .

References:

Arthur D. Little Inc., 1981. Formaldehyde concentration level control in mobile homes[R]. A report to the HCHO Institute by Arthur D. Little Inc., Cambridge, MA.

Boccuzzi F, Chiorino A, Manzoli M, 2003. FTIR study of methnol decomposition on gold catalyst for fuel cells[J]. J Power Sources, 118: 304—310.

Collins J J, Ness R, Tyl R W *et al*., 2001. A review of adverse pregnancy outcomes and formaldehyde exposure in human and animal studies [J]. Toxicology and Pharmacology, 34: 17—34.

Cordi E M, Falconer J L, 1997. Oxidation of volatile organic compounds on an Ag/Al_2O_3 catalyst[J]. Appl Catal. A151: 179—191.

Eriksson B, Johnanssin L, Svedung I, 1980. Filtration of formaldehyde contaminated indoor air[M]. In: The nordest symposium on air pollution abatement by filtration and respiratory protection. Copenhagen.

Liu F Z, Yang M M, Zhou W *et al*., 2003. In situ transmission difference FTIR spectroscopic investigation on anodic oxidation of methanol in aqueous solution [J]. Electro Chem Comm, 5: 276—282.

Millar G J, Rochester C H, Waugh K C, 1995. An FTIR study of the adsorption of formic acid and formaldehyde on potassium-promoted Cu/SiO_2 catalysts[J]. J Catal, 155: 52—58.

Popova G A, Chesalov Y A, Andrushkevich T V *et al*., 2000. Determination of surface intermediates during the selective oxidation of formaldehyde over V-Ti-O catalyst by *in situ* FTIR spectroscopy[J]. J Mole Catal, 158: 345-348.

Sciré S, Minicò S, Crisafulli C *et al*., 2003. Catalytic combustion of volatile organic compounds on gold/cerium oxide catalysts [J]. Appl Catal, B40: 43—49.

Sciré S, Minicò S, Crisafulli C *et al*., 2001. Catalytic combustion of volatile organic compounds over group IB metal catalysts on Fe_2O_3 [J]. Catal Commu, 2: 229—232.

Sekine Y, Nishimura A, 2001. Removal of formaldehyde from indoor air by passive type air-cleaning materials [J]. Atmospheric Environmental, 35: 2001—2007.

Spivey J J, 1987. Complete catalytic oxidation of volatile organics[J]. Ind Eng Chem Res, 26: 2165—2180.

Yu C, Crump D, 1998. A review of the emission of VOCs from polymeric materials used in buildings[J]. Building and Environmental, 33: 357—374.