Perfect catalytic oxidation of formaldehyde over a Pt/TiO₂ catalyst at room temperature

Changbin Zhang^a, Hong He^{a,*}, Ken-ichi Tanaka^b

^a State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, PO Box 2871, Beijing 100085, PR China

^b Saitama Institute of Technology, 1690 Fusaiji, Okabe, Saitama, Japan

Received 25 October 2004; accepted 23 December 2004

Available online 18 January 2005

Abstract

A 1 wt% Pt/TiO₂ catalyst was prepared and tested for the catalytic oxidation of formaldehyde (HCHO) at room temperature. The results of activity tests showed that HCHO can be completely oxidized over the Pt/TiO₂ catalyst in the space velocity of GHSV = 50,000 h⁻¹ at room temperature. A mass balance study proved that HCHO selectively oxidized into CO₂ and H₂O over Pt/TiO₂ at room temperature. No by-products were found in the effluent gases. The XRD patterns indicated that platinum is in a very high dispersion degree on TiO₂.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Formaldehyde; Pt/TiO₂; Catalytic oxidation; Room temperature; Mass balance

1. Introduction

Formaldehyde (HCHO) emitted from newly developed building materials, plastic cements and paintings is a noxious organic compound of the indoor environment [1], which brings about sick even at concentration lower than ppm. Therefore, the abatement of it at room temperature is a problem which should be urgently solved.

A number of studies, related to the removal of HCHO by adsorbents, have been studied both in the lab and in the field. In some cases, these absorbents successfully reduced indoor concentrations of HCHO at field test. However, the effectiveness of the removal materials was limited for a short period due to their removal capacities.

Catalytic oxidation is a promising technology for the abatement of emission of VOCs, because VOCs

can be oxidized to CO₂ over catalysts at much lower temperatures than those of thermal oxidation [3–5]. For catalytic oxidation reaction, the supported noble metals (Au, Pt, Pd, Rh, Ag) catalysts [4–10] or metal oxides (Cu, Cr, Mn) [11–15] are the conventional catalysts. Imamura et al. [10] have found that silver–cerium composite oxide was active for oxidative decomposition of HCHO above 150 °C. Recently, Álvarez et al. [11] have reported that HCHO could be completely oxidized into CO₂ and H₂O over 0.4 wt% Pd–Mn/Al₂O₃ above 90 °C. If catalytic oxidative decomposition of VOCs occurs over some catalysts at room temperature, the process can be very useful for the removal of indoor HCHO without thermal and energy sources. Although, VOCs combustion has been widely investigated using many materials as catalysts, the development of a total oxidation catalyst for HCHO decomposition at room temperature is still a challenging subject to be solved. Up to now, little work on the catalytic oxidation of HCHO into CO₂ at room temperature has been reported.

* Corresponding author. Tel.: +86 10 62849123; fax: +86 10 62923563.

E-mail address: honghe@mail.rcees.ac.cn (H. He).

The present work reports a catalyst over which HCHO can be completely oxidized into CO_2 and H_2O at room temperature. The catalyst was also characterized by BET and XRD methods.

2. Experimental

2.1. Catalyst preparation

The supported catalysts, Pt/TiO_2 , were prepared by an impregnation method with an aqueous solution of H_2PtCl_6 , and the excessive water was removed in a rotary evaporator at 80°C until dryness. The wet sample was dried at 110°C for 12 h and then calcined at 400°C for 2 h. Platinum loading was 1 wt%.

2.2. Catalysts characterization

The nitrogen adsorption–desorption isotherms were obtained at -196°C over the whole range of relative pressures, using a Micromeritics ASAP 2100 automatic equipment. Specific areas were computed from these isotherms by applying the BET method. The fresh catalysts were characterized by X-ray diffractometry using a computerized Rigaku D/max-RB X-Ray Diffractometer (Japan, $\text{Cu K}\alpha$ radiation, 1.54056 nm).

2.3. Catalytic tests

The activity tests for the catalytic oxidation of HCHO over catalyst were performed with a fixed-bed quartz flow reactor (length = 300 mm, diameter = 4 mm) by passing a gas mixture of $\text{HCHO/O}_2/\text{He} = 100\text{ ppm}/20\text{ vol\%/balance}$ at a total flow rate of $50\text{ cm}^3\text{ min}^{-1}$ (GHSV: 50,000, 100,000, 200,000 h^{-1} by changing the used catalyst volume) at room temperature (25°C). HCHO standard gas was constantly introduced from a gas-generator system [2]. The HCHO, CO and CO_2 were analyzed using a gas chromatograph (GC) equipped with

hydrogen flame ionization detector (FID) and Ni catalyst converter which was used for converting the carbon oxides quantitatively into methane in the presence of hydrogen before the detector. Separations were carried out using two columns: a carbon molecular sieve column for permanent gases (CO and CO_2) and a GDX-403 column for the HCHO. The operating parameters were as follows: temperature of the detector, 180°C ; temperature of the column, 50°C ; carrier gas, helium 30 ml min^{-1} ; volume of the analyzed sample, 1 ml. In addition, the effluent gas was monitored by an on-line quadrupole mass spectrometer (Agilent, 5973N).

3. Results and discussion

Specific area of the Pt-loaded catalyst decreased, as expected, with respect to the bare TiO_2 (Table 1). The decrease may be caused by calcination of TiO_2 at 400°C . In addition, Pt-particles might block pores of TiO_2 , which would also lead to the reduction of specific surface area after Pt deposition.

Catalyst structures were revealed by XRD. Fig. 1 shows the diffraction patterns of TiO_2 and Pt/TiO_2 catalysts. The lines were indexed to TiO_2 (PDC84-1285, PDC84-1286). XRD pattern of the Pt/TiO_2 catalyst was essentially the same as that of the TiO_2 sample. The absence of diffraction lines of platinum on Pt/TiO_2 catalyst indicates that platinum is in a very high dispersion degree. As the lower detection limit of the X-ray technique is around 4 nm, it is inferred that crystal sizes of platinum phases are below that value.

Table 1
Specific area of titanium oxide and Pt-loaded titanium oxide catalysts

Sample	BET area ($\text{m}^2\text{ g}^{-1}$)
TiO_2	102
Pt/TiO_2	55

Fig. 1. X-ray diffraction patterns of TiO_2 and Pt/TiO_2 catalysts.

Fig. 2. HCHO conversions as a function of reaction time on Pt/TiO_2 at room temperature with different GHSV $50,000\text{ h}^{-1}$ (■), $100,000\text{ h}^{-1}$ (●), $200,000\text{ h}^{-1}$ (▲). Reaction conditions: HCHO 100 ppm, O_2 20 vol%, He balance. Total flow rate: $50\text{ cm}^3\text{ min}^{-1}$.

Table 2

Mass balance table of the activity test over Pt/TiO₂ (at room temperature)

Gas	SV = 50,000 h ⁻¹			SV = 100,000 h ⁻¹			SV = 200,000 h ⁻¹		
	Inlet (ppm)	Outlet (ppm)	Yield ^a (%)	Inlet (ppm)	Outlet (ppm)	Yield ^a (%)	Inlet (ppm)	Outlet (ppm)	Yield ^a (%)
HCHO	102	0	–	101	3	–	102	43	–
CO ₂	5.2	107.2	100	4.9	103.6	99.7	4.8	63.7	99.8
CO	3.2	3.2	–	2.9	2.9	–	2.4	2.4	–

^a Yield (%) = $\Delta\text{CO}_2(\text{ppm}) \cdot 100/\Delta\text{HCHO}(\text{ppm})$, $n = 10$.

Fig. 2 shows the conversions of HCHO at room temperature as a function of reaction time over Pt/TiO₂ in the space velocity of GHSV = 50,000, 100,000 and 200,000 h⁻¹. It was clear that Pt/TiO₂ shows a extremely high activity for HCHO oxidation at room temperature; 100% HCHO conversion was attained in the space velocity of GHSV = 50,000 h⁻¹, and about 97% and 58% HCHO conversion in the space velocity of GHSV = 100,000 and 200,000 h⁻¹, respectively. In addition, after the HCHO conversion reached a steady level, there was no indication of deactivation taking place during the period investigated. It must be reminded that pure TiO₂ had no activity for HCHO oxidation under the same experimental conditions.

Fig. 3 shows the time courses of the components of the effluent gases recorded by an on-line MS analyzer while the reaction of HCHO oxidation was performed at room temperature and in the space velocity of GHSV = 50,000 h⁻¹. After switching on the reaction gases, fragmentation intensity of HCHO ($m/z = 29, 30$) gradually decreased to a steady intensity, the fragmentation intensities of CO₂ ($m/z = 44$) and H₂O ($m/z = 18$), which were the reaction products, increased and slowly reached a steady level at last. No by-product was de-

tected in effluent gases by MS, which indicates that CO₂ and H₂O were the only products.

After the HCHO conversions reached a steady level in the space velocity of GHSV = 50,000, 100,000 and 200,000 h⁻¹, the mass balance for the catalytic oxidation of HCHO over Pt/TiO₂ at room temperature was recorded and shown in Table 2. Average values of the 10 runs were described for the different space velocity. As shown in Table 2, when HCHO concentration decreased from 102 ppm to zero in the space velocity of GHSV = 50,000 h⁻¹, 102 ppm CO₂ was produced and yielded 100%. In addition, when HCHO concentrations decreased from 101 (102) to 3 and 43 ppm in the space velocity of GHSV = 100,000 and 200,000 h⁻¹, 98.7 and 58.9 ppm CO₂ was produced and yielded 99.7% and 99.8%, respectively. The CO concentrations did not vary, and no other by-product was detected in effluent gases. The results show that HCHO selectively decomposed into CO₂ and H₂O over Pt/TiO₂ at room temperature.

Acknowledgements

This work was financially supported by the Key Technology R&D Programme of the Ministry of Science and Technology, Peoples Republic of China (Grant 2003A11).

References

- [1] C. Yu, D. Crump, *Build. Environ.* 33 (1998) 357.
- [2] Y. Sekine, A. Nishimura, *Atmos. Environ.* 35 (2001) 2001.
- [3] J.J. Spivey, *Ind. Eng. Chem. Res.* 26 (1987) 2165.
- [4] S. Scire, S. Minicò, C. Crisafulli, C. Satriano, A. Pistone, *Appl. Catal. B* 40 (2003) 43.
- [5] S. Scire, S. Minicò, C. Crisafulli, S. Galvagno, *Catal. Commun.* 2 (2001) 229.
- [6] J.E. Sawyer, M.A. Abraham, *Ind. Eng. Chem. Res.* 33 (1994) 2084.
- [7] P. Papaefthimiou, T. Ioannides, X.E. Verykios, *Catal. Today* 54 (1999) 81.
- [8] W. Wang, H.B. Zhang, G.D. Lin, Z.T. Xiong, *Appl. Catal. B* 24 (2000) 219.
- [9] E.M. Cordi, J.L. Falconer, *Appl. Catal. A* 15 (1997) 179.
- [10] S. Imamura, D. Uchihori, K. Utani, *Catal. Lett.* 24 (1994) 377.

Fig. 3. The time courses of the components of the effluent gases recorded by an on-line MS analyzer. Reaction conditions: HCHO 100 ppm, O₂ 20 vol%, He balance. Total flow rate: 50 cm³ min⁻¹. GHSV: 50,000 h⁻¹.

- [11] M.C. Álvarez, V.A. de la Peña, J.L.G. Fierro, P.L. Arias, *Catal. Commun.* 4 (2003) 223.
- [12] E.M. Cordi, P.J. O'Neill, J.L. Falconer, *Appl. Catal. B* 14 (1997) 23.
- [13] P.O. Larsson, A. Andersson, *Appl. Catal. B* 24 (2000) 175.
- [14] C. Mazzocchia, A. Kaddouri, *J. Mol. Catal.* 204–205 (2003) 647.
- [15] S.C. Kim, *J. Hazard. Mater. B* 91 (2002) 285.