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Catalytic Conversions of Polychlorinated Benzenes and Dioxins with Low-chlorine Using V_2O_5/TiO_2

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Abstract Chlorinated benzene, especially 1,2-dichlorobenzene (1,2-DCB), has been widely used as one of surrogate compounds of dioxin to find the noble methods to control dioxin. However, the relationship between the catalytic activity of dioxin surrogate compound and dioxin has not been understood quite well. In this work, we used a vanadium based catalyst (V_2O_5/TiO_2) to compare catalytic activity of chlorinated benzenes and dibenzo-*p*-dioxins with low-chlorine content using the lab-scale system. We investigated the catalytic conversions of low-chlorinated dioxins, [2-monochlorodibenzo-*p*-dioxin (2-MCDD), 2,3-dichlorodibenzo-*p*-dioxin (2,3-DCDD)] and polychlorinated benzenes [1,2-DCB, 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB), pentachlorobenzene (PeCB), hexachlorobenzene (HCB)] using a V_2O_5/TiO_2 catalyst to understand quantitative relationship between dioxin and benzene with the chlorination level. The catalytic decomposition of chlorinated aromatic compounds was following 1,2-DCB > 1,2,3,4-TeCB > 2-MCDD > PeCB ≥ 2,3-DCDD > HCB. It might be more reasonable that PeCB or HCB should be used as the dioxin surrogate compound rather than 1,2-DCB. Also, we investigated the effect of both O_2 content and space velocity (SV) on the catalytic decomposition of 1,2-DCB in the presence of V_2O_5/TiO_2 catalyst because these factors should be considered significantly in combustion facilities to control various pollutants. The decomposition of 1,2-DCB shows dependency on the SV while the effect of oxygen content on the catalytic decomposition is negligible in the range of 5–20%.

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1 Introduction

It has been reported that polychlorinated dibenzo-*p*-dioxins (PCDDs) are very toxic, carcinogenic, and persistent [1, 2]. The emission of dioxins into the atmosphere is mainly from combustion systems, such as municipal, and industrial incinerators [3–5]. The investigation of efficient technology for the removal of dioxins from flue gas streams has become a matter of urgency [6, 7]. In general, most of municipal solid waste incinerators (MSWIs) are equipped with the facilities, such as electrostatic precipitator, wet scrubber, and selective catalytic reduction (SCR) system in order to remove dust, SO_x, and NO_x. The vanadium pentoxide (V_2O_5) is widely used as SCR catalyst for the removal of NO_x. Recently the V_2O_5/TiO_2 catalyst has been reported to show the catalytic activity for the removal of chlorinated aromatic compounds [6–9]. Various modified vanadium-based catalysts were developed to control dioxin emission in thermal process [10]. However, it is very difficult to treat with dioxin compounds due to toxicity and low-vapor pressure. In general, polychlorinated benzenes have been used as dioxin surrogate compound because of structural similarity [6, 9, 11]. Unfortunately, the quantitative relationship between dioxins and chlorinated benzenes over the V_2O_5/TiO_2 catalyst is still unclear. Therefore, it is encouraged to investigate the catalytic activity of benzene and dioxin with the chlorination pattern toward V_2O_5/TiO_2 catalyst. In this work, we employed four polychlorinated benzenes [1,2-dichlorobenzene (1,2-DCB), 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB), pentachlorobenzene (PeCB), hexachlorobenzene (HCB)] and two

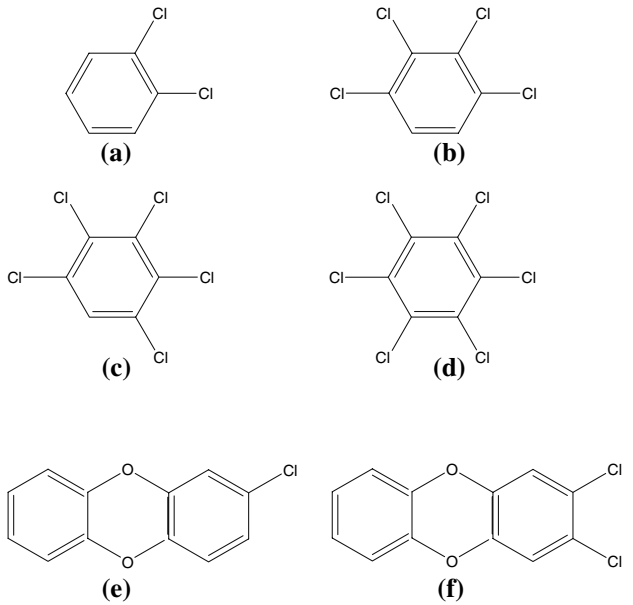

Fig. 1 Molecular structures of 1,2-DCB (**a**), 1,2,3,4-TeCB (**b**), PeCB (**c**), HCB (**d**), 2-MCDD (**e**), and 2,3-DCDD (**f**)

dioxin congeners [2-monochlorodibenzo-*p*-dioxin (2-MCDD), 2,3-dichlorodibenzo-*p*-dioxin (2,3-DCDD)] to compare the catalytic activity over V_2O_5/TiO_2 catalyst. Figure 1 shows the molecular structures of polychlorinated aromatic compounds used in this work.

2 Experimental Section

2.1 Chemicals

2-Monochlorodibenzo-*p*-dioxin and 2,3-DCDD prepared as powder were purchased from AccuStandard to perform the catalytic decomposition. Also, standard solutions of 2-MCDD and 2,3-DCDD were also purchased from AccuStandard to calibrate the gaseous concentration. 1,2-DCB (99%), 1,2,3,4-TeCB (98%), PeCB (98%), and HCB (99%) were purchased from Aldrich, St. Louis, MO, USA and used without further purification. The V_2O_5/TiO_2 was synthesized by an impregnation method, using ammonium metavanadate (NH_4VO_3) as V_2O_5 precursor and TiO_2 (Degussa, Germany, P-25). NH_4VO_3 was resolved in oxalic acid at 40 °C and TiO_2 was added into the prepared solution at 80 °C with vanadium content of 1–10 wt.%. The solution including both NH_4VO_3 and TiO_2 was dried in vacuum oven at 50 °C for 1 h after keeping at room temperature for a day. The V_2O_5/TiO_2 catalyst was calcined at 450 °C for 3 h before use. Because the V_2O_5/TiO_2 with a vanadium content of 3.5–5.0 wt.% showed higher activity for the degradation of 1,2-DCB, the 3.5 wt.% V_2O_5/TiO_2 catalyst was used in this work. The BET surface area and total pore volume of 3.5 wt.% V_2O_5/TiO_2 were measure to be 48.7 $m^2\ g^{-1}$ and 0.323 mL g^{-1}, respectively. Figure 2 shows the TEM image of the 3.5 wt.% V_2O_5/TiO_2 catalyst measured by a transmission electron microscope (Philips CM30). The particle size of the catalyst was <50 nm and the average particle size was 25 nm. The distribution of particle size was measured by GAIA blue (Version 5.3) and listed in Table 1. The average pore diameter of V_2O_5/TiO_2 was 265 Å. The O_2 gas of 5, 10, and 20% balanced with N_2 gas were purchased from a Korean company (Shin-yang, Seoul, South Korea). The oxygen gas was used both as a carrier gas to feed the gas sample into the GC inlet and as oxidant of V_2O_5. Three mass flow controllers (MKS) were used to adjust the flue gas flow rate into 30 mL min^{-1}.

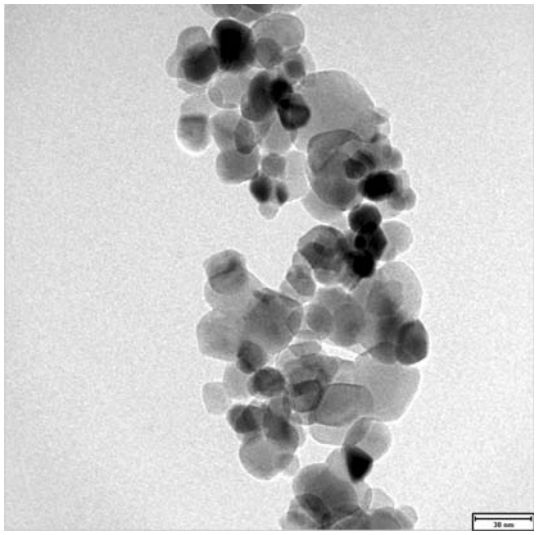

Fig. 2 TEM micrograph of 3.5 wt.% V_2O_5/TiO_2

2.2 Experimental Apparatus

An oil-bath with a temperature programmed controller was used to vaporize the polychlorinated aromatic compounds, 1,2,3,4-TeCB, PeCB, HCB, 2-MCDD, 2,3-DCDD which have low-vapor pressure under mild condition. The sample generator and catalyst bed reactor were made of stainless steel. The amount of V_2O_5/TiO_2 filled into the catalyst bed was 0.1 g and commercial glass wool were used to support the catalyst bed.

A stainless steel tube (1/4 in.) was also used to transfer the gas sample from the sample generator to the GC inlet. The catalytic decomposition of chlorinated compound was performed under the gas hour space velocity (GHSV) of 22,000 or 10,000 h^{-1}. The degradations of 1,2-DCB and 1,2,3,4-TeCB were performed at the catalyst temperatures ranging from 150 to 400 °C, at the intervals of 50 °C. For the catalytic decomposition of PeCB, HCB, 2-MCDD, and

Table 1 Distribution of the particle size for the 3.5 wt.% V_2O_5/TiO_2 catalyst

Size (nm)	10–20	20–30	30–40	40–50
Percent (%)	44	25	25	6

2,3-DCDD the temperature of the catalyst bed was adjusted from 200 to 400 ˚C, at intervals of 50 ˚C. The stainless steel tube was wrapped with heating tape and held at 200 ˚C to avoid condensation. The pyrolysis of 1,2-DCB was also performed in the absence of catalyst to compensate for the catalytic degradation. The concentration of vaporized sample was quantitatively measured using a standard solution. Three adsorbent cylinders, filled with activated carbon, were used to treat the outlet gas.

2.3 Analysis

A gas chromatograph (Agilent 6890N), equipped with a six-port valve (0.25 mL), capillary column [DB-dioxin, 60 m 0.25 mm (i.d.) 0.15 μm (film)], and ^{63}Ni electron capture detector (μ-ECD), was employed for detection of the sample. Injector and detector temperature were set at 275 and 300 ˚C, respectively. The oven temperature washeld at 200 ˚C for 1 min, then increased at a rate of 4 ˚C min^{-1} up to 228 ˚C, and held at 228 ˚C for 1 min.

3 Results and Discussion

3.1 Conversion of 2-MCDD and 2,3-DCDD

Figure 3 shows the catalytic decomposition of gaseous 2-MCDD and 2,3-DCDD by the V_2O_5/TiO_2 catalyst. The 2,3-DCDD is selected to study the catalytic activity of V_2O_5/TiO_2 for the removal of the lateral chlorinated congeners because the lateral chlorinated dioxins such as 2,3,7,8-TCDD are known to be toxic. The concentrations of vaporized 2-MCDD and 2,3-DCDD at 200 ˚C were 0.2 and 0.1 ppm, respectively. In general it is difficult to vaporize dioxin with the increase of chlorination. When the catalyst temperature was adjusted to 400 ˚C, ~80% of the initial 2-MCDD concentration (0.2 ppm) was removed; however, the catalytic degradation of gaseous 2,3-DCDD (0.1 ppm) was <50% under the same condition. As the increase of chlorine the reduction potential of PCDD increases and the oxidative degradation of PCDD is unfavorable. The electron affinity of neutral molecule might be substituted for the term of reduction potential. Based on theoretical studies the (vertical) electron affinities of PCDD were estimated to increase with the level of chlorination [12, 13]. Hence, it is reasonable that the oxidative conversion of 2,3-DCDD is slower than 2-MCDD.

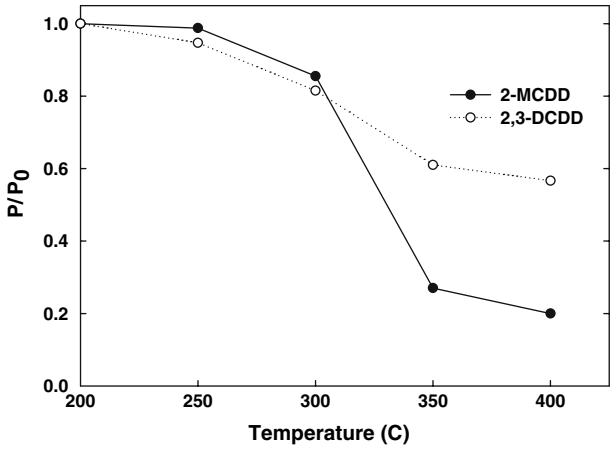

Fig. 3 Catalytic degradations of 2-MCDD (0.2 ppm) and 2,3-DCDD (0.1 ppm) using V_2O_5/TiO_2

3.2 Conversion of Polychlorinated Benzene

We selected polychlorinated benzenes as dioxin surrogate compounds as a model compound of dioxin. The degradations of polychlorinated benzenes, 1,2-DCB, 1,2,3,4-TeCB, PeCB, HCB were carried out in the presence of 3.5 wt.% V_2O_5/TiO_2 catalyst. The vapor pressure of 1,2-DCB at 30 ˚C was measured to be about 2,000 ppm which was similar to the previous work [14]. The vapor pressure of 1,2,3,4-TeCB at 100 ˚C was measured to be 2,000 ppm. The vapor pressures of PeCB and HCB at 100 ˚C were estimated to be 1,660 and 70 ppm, respectively [14, 15]. In Fig. 4, the catalytic degradations of the 1,2-DCB with the concentrations, 20, 200, and 2,000 ppm by V_2O_5/TiO_2 were compared with increasing temperature of catalyst bed. The

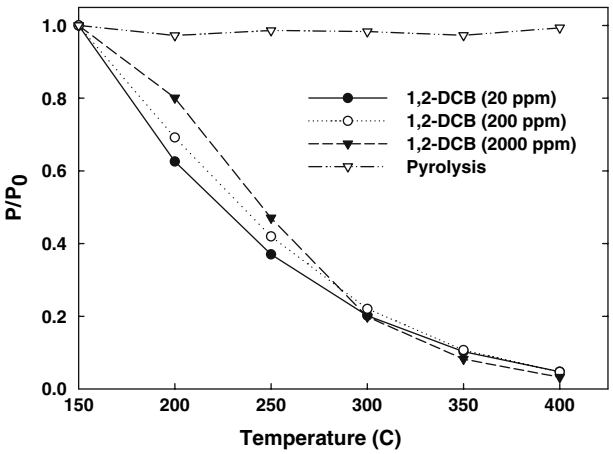

Fig. 4 Catalytic degradation of 1,2-DCB using V_2O_5/TiO_2

degradation of 1,2-DCB by pyrolysis was negligible, as shown in Fig. 4. The conversion of 1,2-DCB was very sensitive to the catalyst bed temperature. When the catalyst bed temperature was below 300 ˚C, the degradation of 1,2-DCB showed a slight concentration dependency. However, when the catalyst bed temperature was above 300 ˚C, there was no great dependency on the concentration of 1,2-DCB.

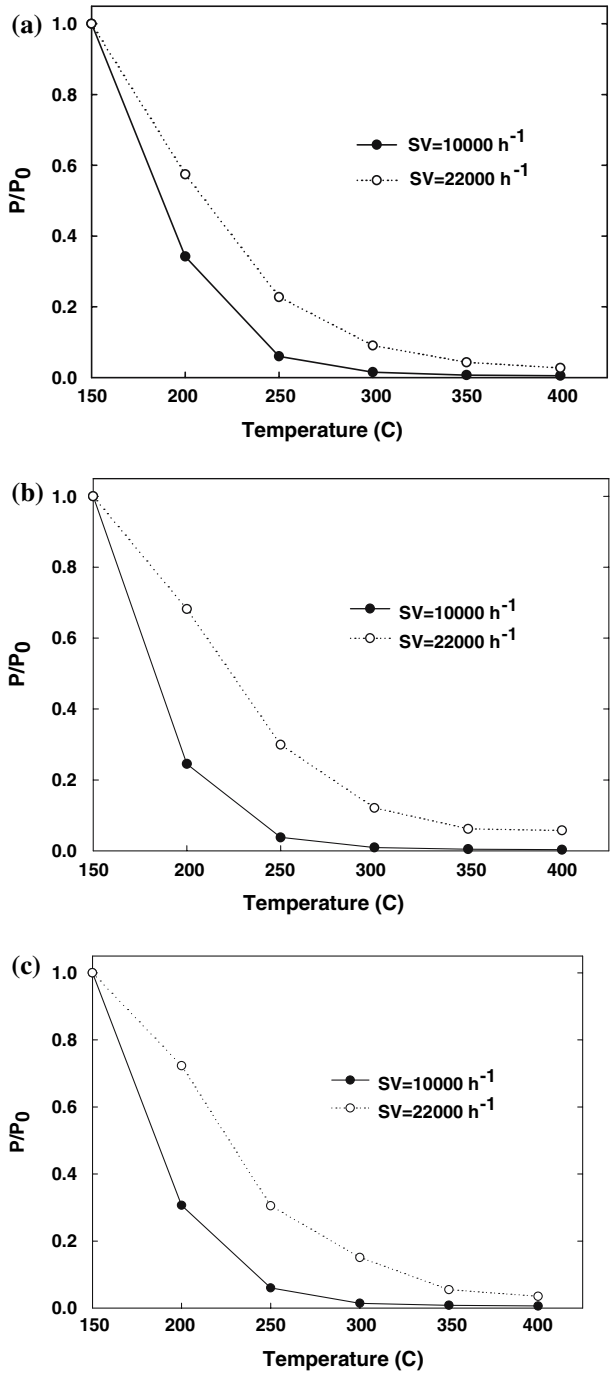

Fig. 5 Catalytic degradation of 1,2-DCB (2,000 ppm) using the V_2O_5/TiO_2 catalyst when the content of O_2 balanced with N_2 was 5% (**a**), 10% (**b**), 20% (**c**)

This result agrees to the previous work [9]. When the temperature of the catalyst bed was set at 400 ˚C, the degradation of 1,2-DCB by 3.5 wt.% V_2O_5/TiO_2 catalyst was >95%, regardless of the initial concentration. It was observed by GC/FID equipped with the Methanizer that the decomposition of 1,2-DCB by 3.5 wt.% V_2O_5/TiO_2 catalyst produced CO and CO_2 more than 95%.

In this work we investigated the effects of space velocity (SV) and oxygen contents on conversion of 1,2-DCB. The SV means the inverse of reaction time on the catalyst surface and can be defined as following equation.

$$\mathrm{SV} = \text{flow rate}/\text{volume of catalyst.}$$

In general, the increase of SV results in reducing the catalytic conversion. Figure 5 shows the conversion of 1,2-DCB according to the SV and oxygen content. Figure 5a compares the conversion of 1,2-DCB in the presence of 5% O_2 when the space velocities of the system set to be 10,000 and 22,000 h^{-1}, respectively. Figure 5b, c show the conversion of 1,2-DCB under the supplied oxygen contents 10 and 20%, respectively. As shown in Fig. 5 the conversion of 1,2-DCB is variable according to the SV while the effect of the oxygen content in the range of 5–20% is negligible.

Figure 6 shows the catalytic conversion of 1,2-DCB, 1,2,3,4-TeCB, PeCB, HCB, 2-MCDD, and 2,3-DCDD over V_2O_5/TiO_2 catalyst. The conversion of 1,2,3,4-TeCB over V_2O_5/TiO_2 decreases slightly in comparison with 1,2-DCB. The catalytic conversions of PeCB and HCB are very low. The conversion of PeCB is similar to the 2,3-DCDD while HCB is slightly lower than 2,3-DCDD. It is no doubt that the reduction potential of chlorinated benzene increases with the chlorination level. The electron affinities of 1,2-DCB, PeCB, and HCB were estimated to be 0.09, 0.73, and

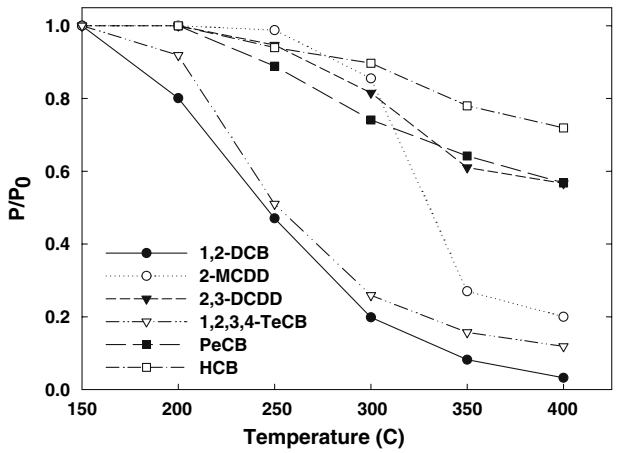

Fig. 6 Catalytic conversion of chlorinated benzenes (2,3-DCB, 1,2,3,4-TeCB, PeCB, and HCB) and low-chlorinated dioxins (2-MCDD and 2,3-DCDD)

1.0 eV, respectively [16–18]. As the reduction potential of polychlorinated aromatic compound increases with the increase of chlorination, the oxidative destruction of chlorinated compound by V_2O_5/TiO_2 is unfavorable.

4 Conclusions

The catalytic conversions of gaseous 1,2-DCB, 1,2,3,4-TeCB, PeCB, HCB, 2-MCDD, and 2,3-DCDD have been performed using the 3.5 wt.% V_2O_5/TiO_2 catalyst to compare the catalytic conversion of dioxin and benzenes with the chlorination level. We did not observe any significant peak of chlorinated compound as an intermediate in GC/μ-ECD during the catalytic decomposition of chlorinated aromatic compound used in this work. There was great difference between 2,3-DCDD and 1,2-DCB toward catalytic conversion by the 3.5 wt.% V_2O_5/TiO_2. The conversion of 2,3-DCDD was similar to PeCB. The conversion of HCB was very low. The decomposition rate of the aromatic compounds including chlorines by the V_2O_5/TiO_2 catalyst was following 1,2-DCB > 1,2,3,4-TeCB > 2-MCDD > PeCB ≥ 2,3-DCDD > HCB. Based on the previous work the decompositions of chlorinated benzenes, 1,2-DCB, 1,2,3-trichlorobenzene, 1,2,4,5-tetrachlorobenzene, and HCB by V_2O_5–WO_3/TiO_2 catalyst decreased with increasing chlorination [19].

Figure 7 shows the Arrhenius plots of polychlorinated benzenes and dioxin. The Arrhenius parameters, activation energy and frequency factor, could be estimated from the inlet equations. The activation energy and frequency factor of 2,3-DCDD are similar to PeCB. Therefore, it might be unreasonable to use 1,2-DCB as dioxin surrogate compound in V_2O_5/TiO_2 employed system. Highly chlorinated benzene such as PeCB or HCB might be better than 1,2-DCB as a dioxin surrogate compound.

Also, we investigated the catalytic conversion of 1,2-DCB according to oxygen contents (5, 10, and 20%) and SV (10,000 and 22,000 h^{-1}) although the variable range was set within narrow limits. There was no great dependency on the oxygen contents for the conversion of 1,2-DCB. However, the conversion of 1,2-DCB showed significant dependency on the SV. The catalytic decomposition of the chlorinated aromatic compounds by V_2O_5/TiO_2 decreased with the chlorination level. This tendency might be due to the degree of the reduction potential.

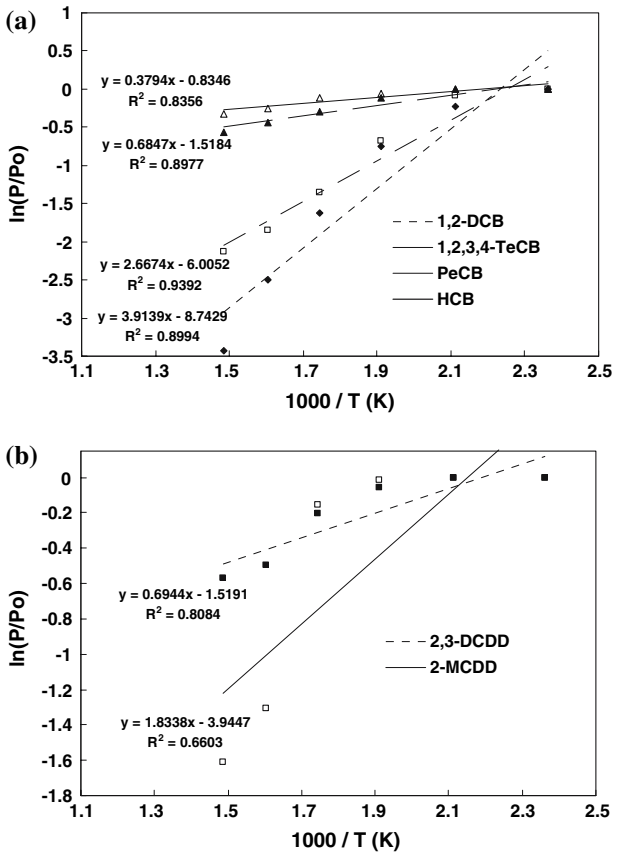

Fig. 7 The Arrhenius plots of $\ln(P/P_0)$ against 1,000/T for the decomposition of polychlorinated benzenes (**a**) and dioxins (**b**)

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References

1. Mhin BJ, Lee JE, Choi W (2002) J Am Chem Soc 124:144–148
2. Lee JE, Choi W, Mhin BJ, Balasubramanian K (2004) J Phys Chem A 108:607–614
3. Lee JE, Choi W, Mhin BJ (2003) J Phys Chem A 107:2693–2699
4. Olie K, Vermeulen PL, Hutzinger O (1977) Chemosphere 8:455–459
5. Katami T, Yasuhara A, Okuda T, Shibamoto T (2002) Environ Sci Technol 36:1320–1324
6. Finocchio E, Busca G, Notaro M (2006) Appl Catal B 62:12–20
7. Liljelind P, Unsworth J, Maaskant O, Marklund S (2001) Chemosphere 42:615–623
8. Goemans M, Clarysse P, Joannes J, Clercq PD, Lenaerts S, Matthys K, Boels K (2004) Chemosphere 54:1357–1365
9. Chung K-S, Jiang Z, Gill B-S, Chung J-S (2002) Appl Catal A 237:81–89
10. Cho C-H, Ihm S-K (2002) Environ Sci Technol 36:1600–1606
11. Lichtenberger J, Amiridis MD (2004) J Catal 223:296–308
12. Lee JE, Choi W, Mhin BJ (2003) Bull Korean Chem Soc 24:792–796
13. Lee JE, Choi W, Odde S, Mhin BJ, Balasubramanian K (2005) Chem Phys Lett 410:142–146
14. Won D, Corsi RL, Rynes M (2001) Indoor Air 11:246–256
15. Shen L, Wania F (2005) J Chem Eng Data 50:742–768
16. Steelhammer JC, Wentworth WE (1969) J Chem Phys 51:1802–1814
17. Knighton WB, Bognar JA, Grimsrud EP (1995) J Mass Spectrom 30:557–562
18. Wiley JR, Chen ECM, Chen ESD, Richardson P, Reed WR, Wentworth WE (1991) J Electroanal Chem Interfac 307:169–182
19. Weber R, Sakurai T, Hagenmaier H (1999) Appl Catal B 20:249–256