



Decomposition of hexachlorobenzene over Al₂O₃ supported metal oxide catalysts

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Abstract

Decomposition of hexachlorobenzene (HCB) was investigated over several metal oxides (i.e., MgO, CaO, BaO, La₂O₃, CeO₂, MnO₂, Fe₂O₃, and Co₃O₄) supported on Al₂O₃, which was achieved in closed system at a temperature of 300°C. Catalysts were prepared by incipient wetness impregnation with different metal oxides loading and impregnating solvents. The decomposition efficiency of different catalysts for this reaction depends on the nature of the metal oxide used, and Al₂O₃ supported La₂O₃ was found to be the most active one. Pentachlorobenzene (PeCB), and all tetrachlorobenzene (TeCB), trichlorobenzene (TrCB), and dichlorobenzene (DCB) isomers were detected after the decomposition reaction, indicating that the decomposition was mainly a dechlorination process. The detection of all lower chlorinated benzenes suggested the complexity of decomposition and the presence of more than one dechlorination pathway.

Key words: dechlorination; hexachlorobenzene (HCB); alumina; metal oxides

Introduction

Hexachlorobenzene (HCB) is an environmentally persistent organic pollutant, which accumulates in fatty tissues and shows carcinogenic and mutagenic activity. Although the production of HCB has been prohibited by the Stockholm Convention, high concentration HCB solid wastes still exist, and may cause unpredictable disasters. These potential risks have prompted researchers worldwide to find clean and effective methods for destroying HCB. Metal oxides and Al₂O₃ supported metal oxide are widely used in the decomposition of persistent toxic substances (Krishnamoorthy *et al.*, 2000; Lichtenberger and Amiridis, 2004; Quan *et al.*, 2005; Ma *et al.*, 2007). Weckhuysen *et al.* (1998) studied the destructive adsorption of CCl₄ on alkaline earth metal oxides. Despite lower activity than precious metals at low temperature, metal oxides are considerably cheaper, allowing a higher catalyst loading, which leads to higher active surface area in the metal oxide bed and makes the metal oxide catalyst only slightly less active than Pt/Al₂O₃ (Wang, 2004). Supported metal oxide catalysts have received considerable attention recently (Pirkanniemi and Sillanpaa, 2002). However, little attention was given to the dechlorination of HCB over Al₂O₃ supported metal oxides, especially lanthanide oxides. In our previous study, we reported a new promising

method that effectively degrades HCB by γ -Al₂O₃ with the surface area of 220 m²/g at a relatively low temperature of 300°C. The decomposition efficiency was achieved to be 94.2%. The decomposition mechanism was pointed out to be mainly a ring-cracking process (Zhang *et al.*, 2008). In this article, we preliminarily focus on the decomposition efficiency and pathways of HCB destruction on alumina supported metal oxides, including alkaline earth metal oxides (MgO, CaO, and BaO), transition metal oxides (MnO₂, Fe₂O₃, and Co₃O₄), and lanthanide oxides (La₂O₃ and CeO₂). The mechanism of decomposition and their pathways compared with pure Al₂O₃ are also discussed.

1 Experimental

1.1 Catalyst preparation

Al₂O₃ was crushed and sieved through a 150-mesh before being used as catalyst support. All catalysts used in this study were prepared by incipient wetness impregnation. Ethanol and water were used as impregnating solution. Metal nitrate salts were used for Mg, Ca, Ba, La, Ce, Mn, Fe, and Co as precursor compounds. All compounds were of analytical grade and were obtained from Beijing Chemical Reagent Company. Impregnated supports were dried at 120°C for 1 h, and the material was heated to 600°C, calcined for 2 h. After calcinations, the samples were ground and sieved through 100–200 mesh

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size grain being collected for the catalytic experiments.

1.2 Dechlorination of HCB

The experiment was carried out in sealed glass ampules (2.0 ml). A 2.0-mg HCB (7,023 nmol) and 200 mg corresponding catalyst were mixed and sealed under air atmosphere. Dechlorination experiments were performed at 300°C for 60 min. Samples after the decomposition experiment were extracted by hexane for GC-MS analysis. All experiments were performed in triplicate to ensure the repeatability of the results.

1.3 Sample analysis

After reaction, the ampule bottle was crushed and extracted by hexane. The extracts were analyzed by an Agilent 6890 gas chromatograph equipped with a HP-5MS capillary column (30 m length, 0.25 mm i.d., 0.25 μm film thickness,) and interfaced to Agilent 5973N MSD (Agilent Technologies, USA). The GC oven temperature was held at 50°C for 2 min, programmed to 130°C at 2°C/min, to 180°C at 5°C/min, and then held for 2 min. The injector, MS source, and MS quadrupole temperatures were 250, 230, and 150°C, respectively. Helium carrier gas flow rate was 1.0 ml/min with a splitless mode. MS monitoring ions for single ion monitoring (SIM) analysis of chlorinated benzenes were m/z : 112 and 114 for monochlorobenzene (MCB); m/z : 146 and 148 for DCB; m/z : 180 and 182 for TrCB; m/z : 214, 216, and 218 for TeCB; m/z : 248, 250, and 252 for PeCB; m/z : 284 and 286 for HCB.

2 Results and discussion

2.1 Yield of dechlorination

The dechlorination efficiency (DE, %) was calculated using the following equation.

$$DE = 1 - \frac{\sum_{i=0}^6 iN_i}{6N_0} \quad (1)$$

where, N_i is the molar number of chlorinated benzene containing i chlorine atoms in the molecule, and N_0 is the initial molar number of HCB. Table 1 shows the calculated DE and the amount of chlorinated benzenes formed after the dechlorination reaction.

2.2 Activity measurement

Supported metal oxide catalysts consisted of an active metal oxide phase dispersed on a high surface area Al_2O_3 . The dispersed metal oxide active phase was typically present as a two-dimensional metal oxide overlayer on the Al_2O_3 surface. At low loading, the metal oxide precursor can be dispersed as isolated metal (monomeric) species. Increased loading leads to the adjoining mono oxo species forming oligomeric or polymeric species via metal-oxygen-metal linkage, and eventually, to surface-bond crystalline metal oxide domains (Fierro, 2006). As seen in Table 1, for most of the catalysts DE could reach higher than 94.2% at 300°C for 60 min, except for CaO/Al_2O_3 . For Al_2O_3 supported alkaline earth metal oxides, the dechlorination activity of HCB decreases in the order: $BaO > MgO > CaO$. The activities of supported transition metal oxides and lanthanide oxides, supported 5% of MnO_2 , Fe_2O_3 , Co_3O_4 , La_2O_3 , and CeO_2 were $\geq 97.6\%$. Our pervious experimental results indicate that DE could reach 94.2% at 300°C for 60 min only using Al_2O_3 as a decomposition material (Zhang *et al.*, 2008). Weckhuysen *et al.* (1998) studied the destructive adsorption of CCl_4 on MgO , CaO , SrO , and BaO . It was found that the activity toward CCl_4 parallels the basicity of the alkaline earth metal oxide. Furthermore, the destruction process is essentially a reaction that requires the continuous renewing of the metal oxide surface by O_2^-/Cl^- exchange. Thus, the mobility of oxygen and chlorine atoms in the bulk of the material becomes important. The DE observed with different metal oxides supported on Al_2O_3 depends on the nature of metal oxides. As given in Table 1, those having only s or p electrons in their valence orbitals, such as CaO and MgO , show lower activity on HCB decomposition,

Table 1 Amount of chloride ion of chlorinated benzenes (nmol) formed in the dechlorination reaction over Al_2O_3 supported catalysts*

Catalyst	MCB	1,4-DCB	1,3-DCB	1,2-DCB	1,3,5-TrCB	1,2,4-TrCB	1,2,3-TrCB	1,2,3,5-TeCB	1,2,4,5-TeCB	1,2,3,4-TeCB	PeCB	HCB	Total Cl ion	DE (%)
5% MgO	ND	2.7	30.9	ND	46.5	ND	ND	ND	ND	ND	92.0	1058.5	1230.6	97.1
5% CaO	ND	ND	168.8	ND	209.1	199.3	ND	364.7	341.3	ND	2989.5	3625.9	7898.6	81.3
5% BaO	ND	ND	ND	ND	ND	2.7	ND	14.0	12.9	5.3	83.9	32.9	151.7	99.6
5% MnO ₂	ND	ND	ND	ND	ND	11.8	1.0	80.1	69.1	37.6	375.3	132.1	707.0	98.3
5% Fe ₂ O ₃	ND	8.6	2.3	4.5	ND	19.8	ND	6.9	8.8	6.9	222.6	459.5	739.9	98.2
5% Co ₃ O ₄	ND	0.8	6.0	ND	10.8	ND	ND	17.4	17.7	18.8	212.2	201.1	484.8	98.8
5% La ₂ O ₃	ND	ND	6.1	ND	8.6	8.4	ND	14.0	14.9	13.7	102.9	266.7	435.3	99.0
5% CeO ₂	ND	3.6	ND	1.1	ND	ND	ND	26.5	24.0	8.9	494.3	445.2	1003.6	97.6
10% MgO	ND	2.2	16.6	ND	30.7	ND	ND	31.6	32.9	31.5	149.8	518.9	814.2	98.1
10% CaO	ND	ND	800.7	ND	1027.8	ND	ND	ND	ND	ND	1965.3	25572.5	29366.3	30.3
10% BaO	ND	ND	ND	ND	ND	4.5	ND	107.4	84.6	20.8	385.4	74.9	677.6	98.4
10% MnO ₂	ND	ND	ND	ND	ND	6.5	0.5	38.7	34.7	18.2	122.3	19.5	240.4	99.4
10% Fe ₂ O ₃	ND	27.0	7.3	12.3	ND	35.2	ND	15.7	17.6	19.0	342.9	2427.8	2904.8	93.1
10% Co ₃ O ₄	ND	5.2	52.4	3.2	56.4	45.2	ND	62.9	63.2	64.2	319.6	1099.1	1771.4	95.8
10% La ₂ O ₃	ND	ND	ND	ND	2.2	3.2	ND	15.7	16.1	7.3	85.7	5.7	135.9	99.7
10% CeO ₂	ND	2.6	0.9	1.3	ND	2.6	ND	2.7	3.3	1.7	100.5	242.4	358.0	99.2

* Initial amount of HCB was 7,023 nmol. MCB: monochlorobenzene; DCB: dichlorobenzene; TrCB: trichlorobenzene; TeCB: tetrachlorobenzene; PeCB: pentachlorobenzene; HCB: hexachlorobenzene; DE: dechlorination efficiency. ND: not detected. The detection limits for DCB, TrCB, TeCB, PeCB, and HCB were 0.8, 0.3, 0.2, 0.2, and 0.1 nmol, respectively.

while those having d or f outer electrons (transition metal and lanthanide metal) show a higher HCB decomposition activity. The DE of supported BaO was comparative with transition metal oxides and lanthanide oxides probably owing to the large atom radius of barium, which has a similar electronic shell with transition metals. DE was also influenced by the metal loading of catalysts. DE increased with the metal loading of lanthanide oxides, but for most of the alumina support alkaline earth metal oxides and transition metal oxides, DE decreased with the metal loading, especially for alumina supported CaO. Similar result was also reported by Kim *et al.* (2002), who investigated supported transition metal oxides on catalytic oxidation of toluene, and concluded that the distribution of metal on support was rather important than the specific surface area of the catalyst for the catalyst activity. Krishnamoorthy (2000) observed the same result on Co₃O₄/TiO₂ catalytic oxidation of 1,2-dichlorobenzene, and suggested that the low activity could be attributed to the slow removal of Cl⁻ from the surface of the catalyst and, hence the blockage of the active sites by Cl⁻.

The high DE of Al₂O₃ supported metal oxides catalysts was also investigated using water as an impregnating solvent. Fig.1 shows the comparison of dechlorination efficiency of alumina supported metal oxide catalysts prepared with different impregnating solvents (ethanol and water). As demonstrated in Fig.1, the DE of supported La₂O₃, Co₃O₄, and Fe₂O₃ was almost not influenced by the impregnating solvent. This is probably owing to the high solubility of these metal nitrate salts, that is to say, water can displace ethanol for the preparation of these catalysts in practice. Catalysts such as Al₂O₃ supported MgO, CeO₂, and MnO₂ prepared in water have lower DE than those prepared in ethanol, which is probably owing to the poor dispersion of metal oxides (Carvalho *et al.*, 2001).

2.3 Decomposition mechanisms and pathways of HCB

In our previous study, we proposed that the decomposition of HCB on γ -Al₂O₃ was mainly a ring-cracking process, which was related to the surface character of alumina (Zhang *et al.*, 2008). As well known, the surfaces of alumina are terminated with an oxygen layer, and it

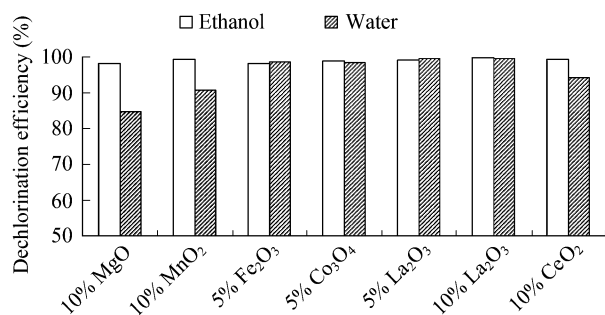


Fig. 1 Comparison of the dechlorination efficiency of alumina supported metal oxide catalysts prepared with different impregnating solvents (ethanol and water).

is covered with hydroxyl groups to neutralize the surface charge according to Pauling's electrostatic valence rule (Ballinger and Yates, 1992). Adulterate alumina with other metal oxides will improve the defect of catalysts, which will influence the properties of alumina, such as the amount of hydroxyl group, and cracking and hydrodechlorination activity. These complex and poorly understood surfaces usually lead to a variety of chemical interaction pathways. Tanaka (2003) reported that the mechanochemical decomposition of trichlorobenzene on CaO was not dehydrochlorination but dechlorination; similar conclusion was also drawn by Krishnamoorthy (2000). However, the oxidation process also existed during the decomposition of chlorinated aromatic compounds. Lichtenberger and Amiridis (2004) investigated the oxidation of chlorobenzene, dichlorobenzene, cyclohexyl chloride, and benzene over V₂O₅/TiO₂ catalysts, and pointed out that the first step of oxidation was the adsorption of the aromatic compound on the catalyst via a nucleophilic attack on the chlorine position in the aromatic ring, followed by the subsequent oxidation of the remaining aromatic ring. Ma *et al.* (2005, 2007) showed that Ca-Fe composite oxides are able to destroy HCB, and pointed out that two competitive reactions hydrodechlorination and the oxidation of aromatic rings took place during the decomposition process. From the analytical results of intermediate chlorobenzenes in Table 1, it was found that HCB, PeCB, and all TeCB, TrCB, DCB-isomer were detected. The decreasing order of TeCB by amount was in order 1,2,3,5- \approx 1,2,4,5- > 1,2,3,4-. The distribution patterns of TrCB and DCB were more

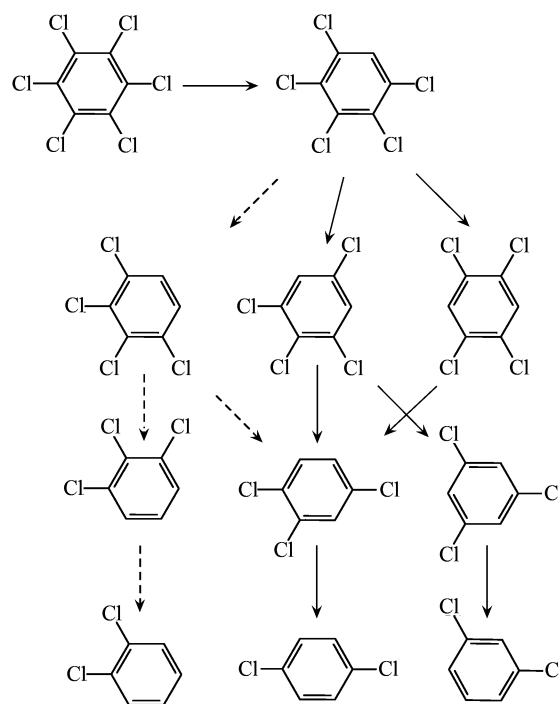


Fig. 2 Observed pathway of HCB dechlorination over Al₂O₃ supported metal oxides. Solid arrows represent the major pathway; dashed arrows represent the other pathway.

complex, 1,2,4-TrCB, 1,3,5-TrCB, 1,4-DCB, and 1,3-DCB were the most abundant ones. Furthermore, the amount of 1,4-DCB and 1,3-DCB changes with the 1,2,4-TrCB, and 1,3,5-TrCB, respectively. 1,2,4-TrCB and 1,4-DCB were the main chlorobenzenes for catalysts such as alumina supported MnO₂, CeO₂, Fe₂O₃, and BaO. Nevertheless, 1,3,5-TrCB and 1,3-DCB were predominant in the tri- and di-chlorobenzene for supported CaO, MgO, Co₃O₄, and La₂O₃. The amount of mono-chlorobenzene was below the detection limit. Based on the experimental results, possible dechlorination pathways of HCB are demonstrated in Fig.2.

The pathway (HCB→PeCB→1,2,3,5-TeCB, 1,2,4,5-TeCB→1,2,4-TrCB→1,4-DCB) was the major pathway for MnO₂, CeO₂, Fe₂O₃, and BaO. The similar conclusion was also made by Fennell (2004) using *Dehalococcoides ethenogenes* strain 195 as a reductive dechlorination substance. However, the finding is the reverse of that in a previous study on reductive dechlorination of HCB using bacterium DF-1, which described the pathway as HCB→PeCB→1,2,3,5-TeCB→1,3,5-TrCB→1,3-DCB (Wu *et al.*, 2002). Nevertheless, this pathway was similar to that of supported CaO, MgO, Co₃O₄, and La₂O₃ in this study. It was evident that HCB decomposition over Al₂O₃ supported metal oxide catalysts was mainly a dechlorination process, which was different from our previous study that decomposition of HCB on γ -Al₂O₃ was mainly a ring-cracking process. Our experimental results suggest that further validation of the existence of the two reactions is needed.

3 Conclusions

Al₂O₃ supported MgO, CaO, BaO, La₂O₃, CeO₂, MnO₂, Fe₂O₃, and Co₃O₄ catalysts were investigated on the decomposition of HCB. For most of the catalysts dechlorination efficiency could reach higher than 94.2% at 300°C for 60 min, except for CaO/Al₂O₃. The catalysts activity of alumina supported metal oxides on the decomposition of HCB was in the order: lanthanide metal \approx transition metal > alkaline earth metal. Al₂O₃ supported La₂O₃ was the most active one. Water could displace ethanol for the preparation of some catalysts, such as La₂O₃, Fe₂O₃, and Co₃O₄ when in practice. The HCB decomposition over Al₂O₃ supported metal oxide catalysts was mainly a dechlorination process.

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