SYNERGISTIC CATALYTIC EFFECT OF METAL OXIDES ON THE LOW-TEMPERATURE DECHLORINATION OF HEXACHLOROBENZENE

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Abstract

Dechlorination of hexachlorobenzene (HCB) was achieved by metal oxides (CaO, PbO, CuO, Cr_2O_3, Fe_2O_3) and their mixtures in a closed systems at temperature of 300 ^oC, which exhibited a synergic effect compared to metal oxides alone, and the positive synergic effect was universal for the mixture of two or more metal oxides. The dechlorination efficiency of HCB by metal oxides followed the order PbO > CuO > Cr_2O_3 > CaO > Fe_2O_3. The high activity of PbO was surprising, which the efficiency of dechlorination reached over 90% after 1 h reaction at 300 ^oC. The mixture of CaO and Fe_2O_3 dramatically enhanced the dechlorination reaction, which the dechlorination efficiency of HCB reached 99.1% at 300 ^oC for 1 h. The main dechlorination pathway of HCB was investigated.

Introduction

It has become an increasingly important issue to remove halogenated aromatic compounds from the environment for their environmentally persistent and carcinogenic activity. It is well known that fly ash contains a multitude of metal oxides with a known effect in both halogenation and dehalogenation reactions as catalysts or promoters[1-4]. Few studies were performed concerning the synerigistic effect of metal oxides in fly ash on dehalogenation reactions. The aim of this investigation was to find less expensive metal oxides as catalysts for chlorinated aromatic compounds destruction, and to examine the synergistic catalytic behavior of metal oxides on the low-temperature dechlorination of hexachlorobenzene as a model compound.

Materials and Methods

Approximately 60 mg of metal oxides (or metal oxide mixtures) which spiked with 300 μg HCB in soda glass ampules (volume, 1.5 ml) were used in all experiments. The ampules were sealed with atmospheres of air and placed in the furnace, and treated under certain conditions. After finishing the dechlorination reaction, the glass tubes were carefully crushed and ultrasonic extracted with 15 ml hexane twice for 15-20 min each time. The solutions were filtered and then used for the measurement of parent HCB remaining and lower chlorinated benzenes newly formed. The analyses of chlorobenzenes were performed by an Agilent 5890 gas chromatograph equipped with a DB-5 capillary column (30 m × 0.25 mm × 0.25 μm). The experimental design was reported in Table 1.

Results and Discussion

The HCB dechlorination efficiency (DE) can be calculated using Eq. (1).

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

Where N_i is the molar mass of chlorinated benzene containing i chlorine atoms in the molecule, and N_0 is the initial molar mass of HCB. The catalytic effect of different metal oxides on HCB dechlorination was shown in Figure 1. The dechlorination efficiencies of HCB by CaO, PbO, CuO, Cr_2O_3 and Fe_2O_3 reached 26.8%, 98.8%, 65.7%, 43.2% and 5.6% at 300 ^oC for 1 h, respectively. The results showed that PbO exhibited notable effect in enhancing HCB dechlorination, and the residual amount of HCB was only 1.8 nmol (see Table 2). The dechlorination efficiencies of HCB by Fe_2O_3 and CaO were below 30%, which were less than other metal oxides. From the Figure 2, CaO was more effective at enhancing the HCB dechlorination reaction when it coexisted with CuO or Fe_2O_3 than with other metal oxides. Especially, dechlorination efficiency of HCB increased greatly when CaO and Fe_2O_3 coexisted, which reached 99.1%. The residual amount of HCB was only 0.8 nmol (see Table 2), much less than the original 1205.9 nmol. As shown in Figure 2 and Figure 3, Cr_2O_3 did not provide the effective synerigistic catalytic dechlorination mixing with other metal oxides. On the other hand, Cr_2O_3 and the mixture of CaO and Fe_2O_3 exhibited a negative synerigistic catalytic effect on the dechlorination of HCB, which the dechlorination efficiency decreased from 90% to 80% (Figure 3). The dechlorination efficiencies of HCB by the mixture of two or more metal oxides except for the mixture containing Cr_2O_3 were all reached above 90% (the results were omitted), which showed positive synergic effect was universal. The intermediates formed in the experiments were given in Table 2. Decreasing orders of chlorobenzenes by amount were 1,2,3,5- > 1,2,4,5- > 1,2,3,4- for tetrachlorobenzenes; 1,2,4- > 1,3,5- > 1,2,3- for trichlorobenzenes. And note that the main catalytic dechlorination pathway were same by different metal oxides or their mixtures, which was
HCB → PeCB → 1,2,3,5 TeCB → 1,2,4 TrCB → DCB. Thought the degradation pathways were not significantly influenced by metal oxides catalyst.

References

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Table 1. Experiment Conditions

run	CaO (mg)	PbO (mg)	CuO (mg)	Cr_2O_3 (mg)	Fe_2O_3 (mg)
1	60	0	0	0	0
2	0	60	0	0	0
3	0	0	60	0	0
4	0	0	0	60	0
5	0	0	0	0	60
6	30	30	0	0	0
7	30	0	30	0	0
8	30	0	0	30	0
9	30	0	0	0	30
10	0	30	30	0	0
11	0	30	0	30	0
12	0	30	0	0	30
13	0	0	30	30	0
14	0	0	30	0	30
15	0	0	0	30	30
16	20	20	20	0	0
17	20	20	0	20	0
18	20	20	0	0	20
19	20	0	20	20	0
20	20	0	20	0	20
21	20	0	0	20	20
22	0	20	20	20	0
23	0	20	20	0	20
24	0	20	0	20	20
25	0	0	20	20	20
26	15	15	15	15	0
27	15	15	15	0	15
28	15	0	15	15	15
29	15	15	0	15	15
30	0	15	15	15	15

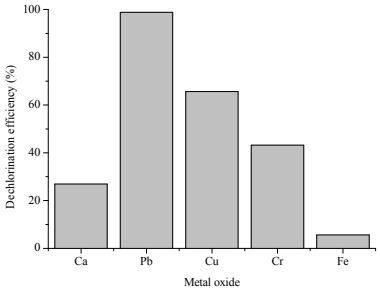

Figure 1. Dechlorination effeciecy on metal oxides (temperature: 300 ^{o}C, time: 1 h, dose: 300 μg HCB/ 60 mg catalyst).

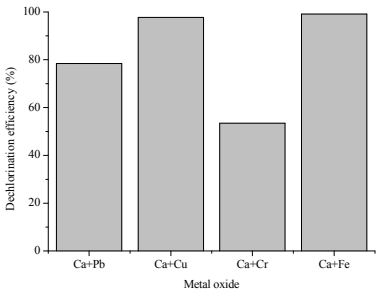

Figure 2. Positive Synergic effect of CaO and other metal oxides on the dechlorination of HCB (temperature: 300 ^{o}C, time: 1 h, dose: 300 μg HCB/ 60 mg catalyst).

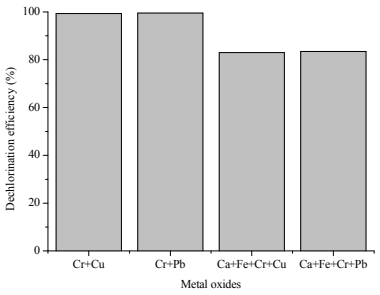

Figure 3. negative synerigistic catalytic effect of Cr_2O_3 and mixture of CaO and Fe_2O_3 on the dechlorination of HCB (temperature: 300 ^{o}C, time: 1 h, dose: 300 μg HCB/ 60 mg catalyst)

Table 2. Comparison of the amount of formed products by metal oxides and mixtures in the dechlorination of HCB (nmol)

Chlorobenzenes	Ca	Pb	Cu	Cr	Fe	Ca+Fe	Ca+Fe+ Cu	Ca+Pb+Cu+Fe
1,3-DCB	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	3.2	2.9
1,4-DCB	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
1,2-DCB	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1.8	< 0.5
1,3,5-TrCB	0.2	< 0.1	18.5	< 0.1	1.4	5.5	< 0.1	0.1
1,2,4-TrCB	1.3	< 0.1	52.2	0.4	7.5	11.1	< 0.1	0.3
1,2,3-TrCB	0.3	< 0.1	0.3	0.1	0.1	0.5	< 0.1	< 0.1
1,2,3,5-TeCB	17.9	1.0	47.1	1.2	1.6	0.4	0.2	0.4
1,2,4,5-TeCB	16.6	0.8	42.6	0.7	1.3	0.2	0.2	0.5
1,2,3,4-TeCB	8.9	0.5	16.1	0.1	0.3	1.0	< 0.1	< 0.1
PeCB	615.7	13.4	179.0	14.6	15.2	0.2	0.0	0.2
HCB	338.9	1.8	158.5	671.5	1116.9	0.8	0.6	0.5