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Competitive Reaction During Decomposition of Hexachlorobenzene Over Ultrafine Ca–Fe Composite Oxide Catalyst

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Abstract The decomposition of hexachlorobenzene (HCB) has been investigated over ultrafine Ca–Fe composite oxide catalyst (Ca/Fe atomic ratio was 3.4), CaO and α-Fe_2O_3 by using in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Adsorption experiments on the surface of oxides monitored by in situ DRIFTS showed that partial oxidation products, i.e., phenolate and acetate species were formed on the surface of Ca–Fe composite oxide. The further studies indicated that Ca–Fe composite oxide catalyst was easier to induce the rupture of C–Cl bond and C–C bond of aromatic rings. The best catalytic activity of Ca–Fe composite oxide may be related to the acidity, which was determined by NH_3–TPD. The products after reaction have been analyzed by XRD and chloride selective electrode. Ca–Fe composite oxide exhibited the highest extent of mineralization for organic chlorine among the different oxides tested. The combined results of current and previous experiments demonstrated that two competitive reactions took place during the decomposition process of HCB: (1) hydrodechlorination resulting in the formation of lower chlorinated benzenes and (2) oxidation of aromatic rings leading to the rupture of aromaticity and the formation of oxidation products. The latter is the major process in the coexisted competitive reaction. A possible decomposition pathway was discussed.

Keywords Competitive reaction · Decomposition · Hexachlorobenzene · Ca–Fe composite oxide · In situ DRIFTS

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1 Introduction

Polychlorinated aromatics are environmentally persistent chemicals, which are recalcitrant toward degradation and show carcinogenic and mutagenic activity [1]. Among them, polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofurans (PCDD/F) are particularly toxic and dangerous for humans and animals. Unfortunately, they can be formed in the bleaching of wood pulp with chlorine-based oxidants, the incineration of chlorine-containing compounds and organic matter, and the recycling of metals. Due to their high toxicity, stringent limits (e.g. 0.1 ng of I-TEQ/Nm^3) have been imposed on the emissions of such compounds in many countries [2]. To meet the standards, various methods have been tried to destroy the chlorinated organics including PCDDs and PCDFs, such as biodegradation [3, 4], photocatalytic oxidation [5, 6] and catalytic hydrodechlorination [7–16].

In seeking to find less expensive reagents for organochlorine destruction, the behavior of CaO, MgO and Fe_2O_3 has been examined respectively [17–19]. Further studies have revealed that the reaction efficiencies can be improved by the presence of a small amount of transition–metal oxide as catalyst coated on nanoparticles. Such ultrafine (nanoscale) particles of metal oxides ([Fe_2O_3]MgO, [Fe_2O_3]CaO, [V_2O_3]MgO) have been synthesized in the form of shell/core-like material [20–22].

As for reaction mechanism, there are two different viewpoints. Stach [9] and Weber [23] et al demonstrated that hydrodechlorination existed, when polychlorinated aromatics was decomposed by different metal oxides. Krishnamoorthy [24–26], Liu [27] and Lichtenberger [28] et al considered that catalytic oxidation was the reaction pathway, when polychlorinated aromatics was decomposed by oxide catalysts.

In our previous work [29], a relatively cheap ultrafine Ca–Fe composite oxide was prepared by using coprecipitation method and used for the decomposition of hexachlorobenzene, which was chosen as a model compound of polychlorinated aromatics. Ca–Fe composite oxide with appropriate composition was proven to possess excellent dechlorination activity at relatively lower temperature. The optimum composition of Ca–Fe composite oxide was confirmed, the Ca/Fe atomic ratio is in the vicinity of 3.4. Ca–Fe composite oxide contained CaO phase and $Ca_2Fe_2O_5$ phase. It was found that the two coexisted phases were beneficial for the dechlorination reaction, showing a remarkable synergic effect. Nonetheless, the detailed reaction mechanism was not clearly understood.

In this article, we investigated the decomposition of HCB over Ca–Fe composite oxide catalyst by in situ DRIFTS spectra. The reaction intermediates was identified, the stability of these species was analyzed. These results combined with those of our previous work provide an insight into the mechanism of HCB decomposition over Ca–Fe composite oxide. For comparing, the decomposition experiments over pure CaO and α-Fe_2O_3 were also carried out respectively.

2 Experimental

Ca–Fe composite oxide (SCF), CaO (SC) and α-Fe_2O_3 (SF) were synthesized, characterized and used to decompose HCB. The detailed description was given in the previous paper [29]. Under simulative reaction conditions, the experiment of in situ DRIFTS was carried out to analyze the intermediate species adsorbed on the oxides. In situ DRIFTS spectra were recorded by a NEXUS 670-FTIR equipped smart collector and a MCT/A detector cooled by liquid N_2. The DRIFTS cell (Nicolet) was equipped with CaF_2 window and a heating cartridge that allowed samples to be heated up. The samples for this study were the mixtures of HCB and catalyst. Prior to each experiment, the catalyst was heated in air for 60 min at 600 °C, and then cooled to room temperature. HCB and pretreated catalyst were finely ground in mass ratio of 20:1, and then placed in a ceramic crucible in an in situ chamber. Spectra of the surfaces of the mixture of HCB and catalyst taken at room temperature were used as the backgrounds for different experiments. All spectra were taken with a resolution of 4 cm^{-1} and an accumulation of 100 scans.

Temperature-programmed desorption of ammonia (NH_3–TPD) was used to characterize the surface acidity of SCF, SC and SF. Prior to the adsorption of NH_3, about 100 mg of sample was pretreated at 500 °C with an Ar flow for 0.5 h and then cooled down to 60 °C. Subsequently, the sample was exposed to flowing ammonia gas mixture (5% NH_3 in Ar) for 0.5 h, then purged by Ar gas for 1 h to excavate physical adsorption of ammonia on catalysts. The NH_3 desorption was conducted between 60 °C and 600 °C at a heating rate of 10 °C min^{-1}. The desorbed ammonia was measured by a TCD (thermal conductivity detector).

The formed Chloride ion (Cl^{-1}) was measured potentiometrically using a chloride selective electrode. The definition used for organic chloride mineralization is as follows:

$$\text{Organic chloride min eralization } \% = \frac{Cl^-}{Cl_0} \times 100$$

Where Cl^- is the molar number of formed chloride anion and Cl_0 is the molar number of chlorine atom from initial HCB.

The new phase formed on the oxide after reaction was identified by X-ray diffractometer (XRD). Diffraction peaks of crystalline phases were compared with those of standard compounds reported in the JCPDS Data File.

3 Results and Discussion

Adsorption and surface reaction studies were carried out using in situ DRIFTS to understand the decomposition process of HCB over different oxides. The measurements were carried out on SCF, SC and SF. A comparison of spectra collected at 300 °C after 30 min in closed systems for the different oxides is attempted in Fig. 1. All the spectra show the presence of a negative and broad valley between 1,603 cm^{-1} and 1,398 cm^{-1}, which can be attributed to overtone bands from C–Cl bending bands of HCB [30]. This indicates that dechlorination is the common results on the three oxides studied. Also seen in all cases are the peak at 1,716 cm^{-1} along with the peaks at 1,439 and 1,575 cm^{-1}. According to previous studies, the band at 1,716 cm^{-1} is assignable to C=O stretching vibration of acetate species [31]. The peaks at 1,575 and 1,439 cm^{-1} are explained by the contribution of C=C stretching vibrations of phenolate species [28, 32, 33]. Phenolate and acetate species are the partial oxidation products when HCB are decomposed, whose appearance provides the proof for the oxidative degradation of HCB. The bands at 2,361 and

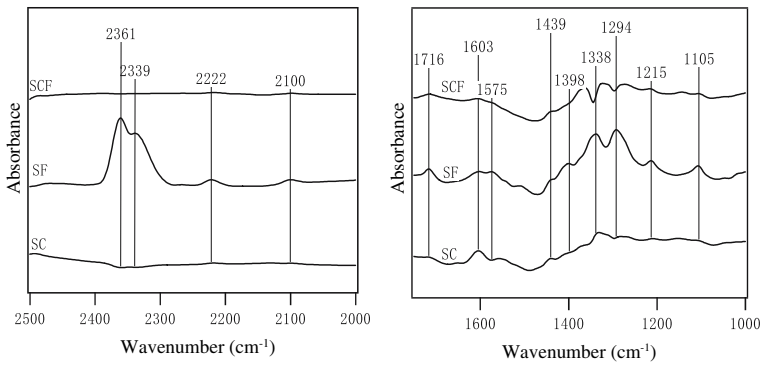

Fig. 1 In situ DRIFTS absorption spectra of HCB on SC, SF and SCF

2,339 cm^{-1} corresponding to CO_2 and the ones at 2,222 and 2,100 cm^{-1} corresponding to CO are observed only in the case of the Fe_2O_3 as compared to the other two oxides. Since CO_2 cannot convert into carbonate, this may lead to the stop of the decomposition of HCB for reaching a chemical equilibrium. Another significant difference among the IR spectra collected on the surface of different oxides is that two strong peaks at 1,338 and 1,294 cm^{-1} were only present on the surface of α-Fe_2O_3. The two peaks corresponding to the stretching of aromatic C=C bonds in the HCB [30] together with other bands from HCB (1,215, 1,105 cm^{-1}) [30] indicate that large amount of HCB adsorbed on the surface of α-Fe_2O_3 after reaction for 30 min. A significant difference between the spectra of Ca–Fe composite oxide and CaO is that the peaks at 1,338 and 1,294 cm^{-1} turn over to negative ones and shift to higher frequencies. This means HCB adsorbed on the surface of composite oxide has almost been decomposed completely. The concentration of acetate on Ca–Fe composite oxide is higher than that on CaO, indicating that formation rate of acetate on Ca–Fe composite oxide is higher than that on CaO. This may lead to better decomposition ability of Ca–Fe composite oxide for HCB.

In situ infrared spectra of SCF collected in our case after 30 min at different temperatures are shown in Fig. 2. At 100 °C, weak peaks corresponding to the ring vibrations of HCB are present, the negative valley between 1,603 and 1,398 cm^{-1} can also be observed, indicating that at this temperature the adsorption and dechlorination of HCB takes place. At 200 °C, we observe remarkable growth of the peaks corresponding to the stretching of aromatic C=C bonds in HCB. Furthermore, the intensity of the negative valley between 1,603 cm^{-1} and 1,398 cm^{-1} increases obviously, indicating that the degree of adsorption and dechlorination of HCB increases at the higher temperature. The amount of surface phenolate and acetate increases with temperature up to 200 °C, and then decreases at 300 °C. This behavior is the result of the increased oxidation activity of SCF at elevated temperatures combined with the lower stability of these species at the higher temperatures. This also indicates that phenolate and acetate are active species on SCF surface, at least at higher temperature. Similar results were reported by Krishnamoorthy et al. They investigated the catalytic decomposition of 1,2-dichlorobenzene over a series of transition metal oxides[26]. Their results of in situ DRIFTS indicate the presence of phenolate and acetate on the surfaces of all catalysts studied under reaction conditions, these surface species were reactive and are potential intermediates. But Krishnamoorthy et al did not concern the possible hydrodechlorination existed when HCB was decomposed. The peaks corresponding to CO appear at 200 °C and disappear

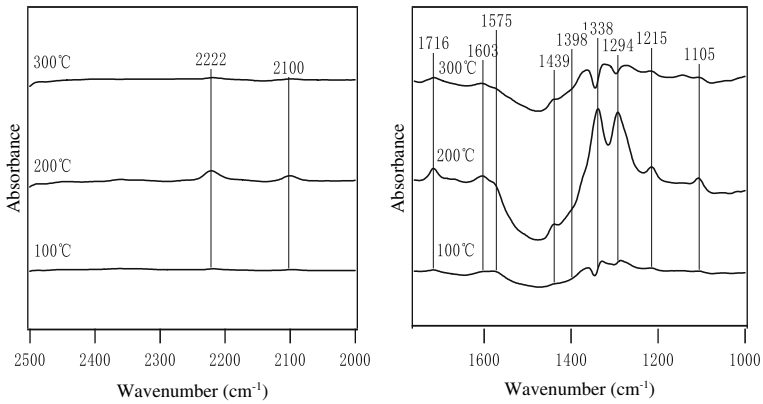

Fig. 2 In situ DRIFTS absorption spectra of SCF collected at 100, 200 and 300 °C in air after 30 min reaction

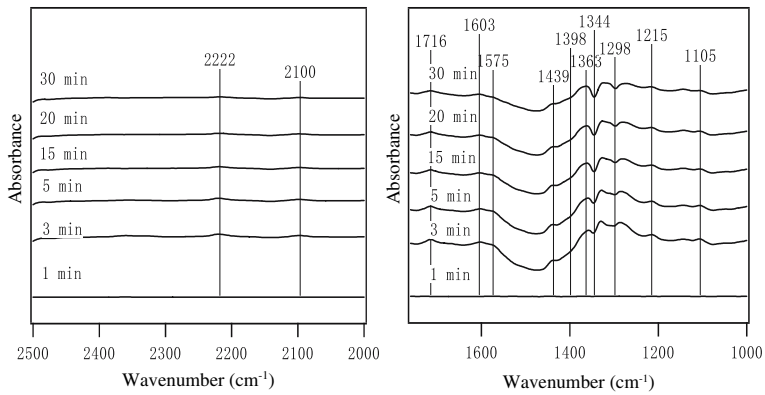

Fig. 3 In situ DRIFTS absorption spectra of SCF collected at 300 °C in air after 1, 3, 5, 15, 20 and 30 min reaction

at 300 °C. After reaction at 300 °C for 30 min, the formed $CaCO_3$ can be confirmed by XRD analysis in Fig. 6. Combined these results, we can draw the conclusion that high temperature is beneficial for the mineralization of HCB over SCF. At 300 °C, the intensity of negative valley between 1,603 cm^{-1} and 1,398 cm^{-1} tends to decrease, this may be the formation of $CaCO_3$ and $CaCl_2$ on the surface of the oxide.

Figure 3. shows the dynamic changes of in situ DRIFTS of SCF as a function of time in air at 300 °C. During the process of dechlorination, the peaks of phenolate, acetate and carbon monoxide species appear in the first 3 min and decrease at longer reaction times, indicating they are partial oxidation products.

Our previous work showed that hydrodechlorination existed in the process of destruction of HCB over SCF, SC and SF [29]. Similar results were also obtained by Stach [9] and Weber [23] et al. The dechlorination efficiency of SCF, SC and SF was 97%, 40% and 50%, respectively. The intermediate products were detected by GC-MS. The formed lower chlorinated benzenes were pentachlorobenzene and tetrachlorobenzene. The analytical result of chloride selective electrode showed that the extent of mineralization of organic chlorine for SCF was 48%.

According to the previous analytical result of XRD, CaO and $Ca_2Fe_2O_5$ coexisted in SCF. The fact that SCF exhibits higher activity than monocomponent oxide may be attributed to the formation of $Ca_2Fe_2O_5$ phase. But the lower chlorinated benzenes detected are in low amounts. There existed discrepancy in the material balance of the starting and dechlorinated materials. This means that hydrodechlorination was not the major pathway when HCB was decomposed.

NH_3–TPD spectra from the surface of three catalysts were compared, as shown in Fig. 4. No desorption peaks were observed in the TPD profiles on SC and SF. This means no acidic sites exist in the single CaO and α-Fe_2O_3. SCF showed two desorption peaks at about 430 and 500 °C, suggesting that two different acidic sites exist in the Ca–Fe composite oxide. Because no acidic sites exist in

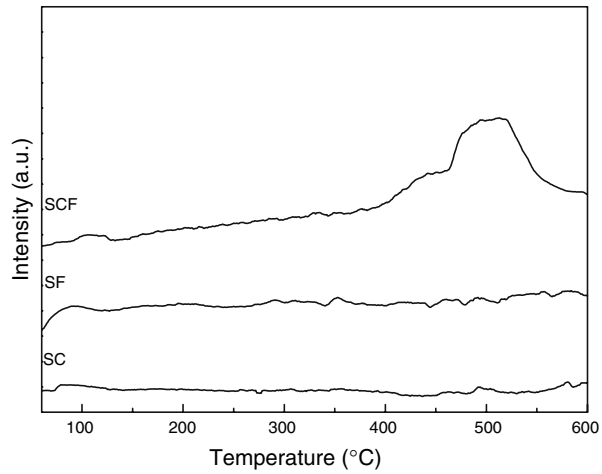

Fig. 4 NH_3–TPD curves for SC, SF and SCF

CaO, the specific acidity in SCF can be attributed to the formed $Ca_2Fe_2O_5$ phase. The appearance of the surface acidity accompanied with the formation of $Ca_2Fe_2O_5$ phase may lead to the best catalytic activity of Ca–Fe composite oxide.

The extent of mineralization of organic chlorine with different oxides was compared and the results were shown in Fig. 5. It was found that after reaction at 300 °C for 30 min, the extent of mineralization of organic chlorine for SC and SF was 18 and 25 respectively, lower than 48% for SCF. It can be seen that there exists larger discrepancy between the declorination efficiency and the efficiency of organic chloride mineralization, indicating that organochlorine atoms were only partially mineralized and were released in the forms of inorganic ions. It can be conjectured that some organochlorine compounds were formed.

The new phase formed on the oxide after reaction at 300 °C for 30 min was identified by XRD and the result was compared with JCPDS database. The XRD pattern (Fig. 6.) showed that $CaCO_3$ (JCPDS file no. 50586) crystal phase was formed after 30 min reaction on SCF and SC. No carbonate was detected on the surface of SF. The

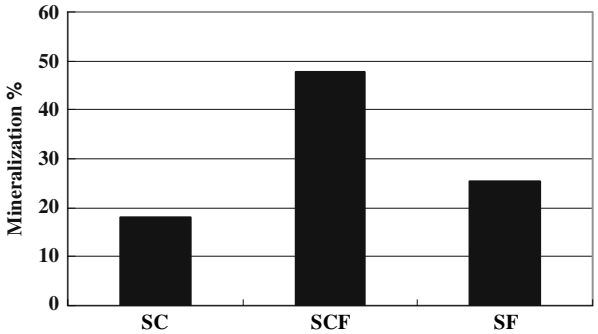

Fig. 5 Comparison of the extent of mineralization (in %) of the different oxides after reaction at 300 °C for 30 min

formation of $CaCO_3$ means the C–C bond breaking of aromatic ring took place and the carbon was oxidized under the reaction conditions. This can also give an explanation for the discrepancy in the material balance of the starting and dechlorinated material. According to the analytical result of Fig. 5, the mineralization of organic chlorine took place on SCF, SC and SF, but no $CaCl_2$ and $FeCl_3$ was detected, this may due to the thorough dispersal of $CaCl_2$ and $FeCl_3$ on the surface of oxides examined.

As mentioned above, hydrodechlorination took place in the destruction of HCB over SCF. But there existed remarkable discrepancy in the material balance of the starting and dechlorinated materials. So we deduce hydrodechlorination was not the major pathway when HCB was decomposed. Based on the results obtained in the current as well as our previous studies, we propose that the decomposition of HCB over SCF proceeds through the mechanism shown in Fig. 7. The oxidation of aromaticity and hydrodechlorination are involved simultaneously in the initial stage of HCB decomposition. The former is the major pathway and the latter is the minor one, because only small amounts of lower chlorobenzenes were detected as the products of hydrodechlorination. Both the two pathways of HCB decomposition lead to the C–Cl bond scission in the beginning of HCB decomposition. The process of hydrodechlorination has been discussed before [9, 29]. The first step of oxidation of HCB is believed to be a nucleophilic substitution. As nucleophile, O^{2-} on the oxide surface is prone to attack aryl halides. Surface phenolates are formed during this step as indicated by the in situ DRIFTS results. The second step of the pathway is the subsequent oxidation of the aromatic ring, leading to the breaking of aromatic ring and the formation of partial oxidation products, i.e. acetates, which can undergo further reaction to form the gas-phase reaction products, such as CO, CO_2. Finally, CO_2 react with oxide and produce $CaCO_3$. During the decomposition of HCB, organochlorine atoms are mineralized and released in the forms of chlorine ions.

4 Conclusions

An in situ DRIFTS investigation of the decomposition of HCB has been carried out over Ca–Fe composite oxide, CaO and α-Fe_2O_3. In situ DRIFTS studies indicate the

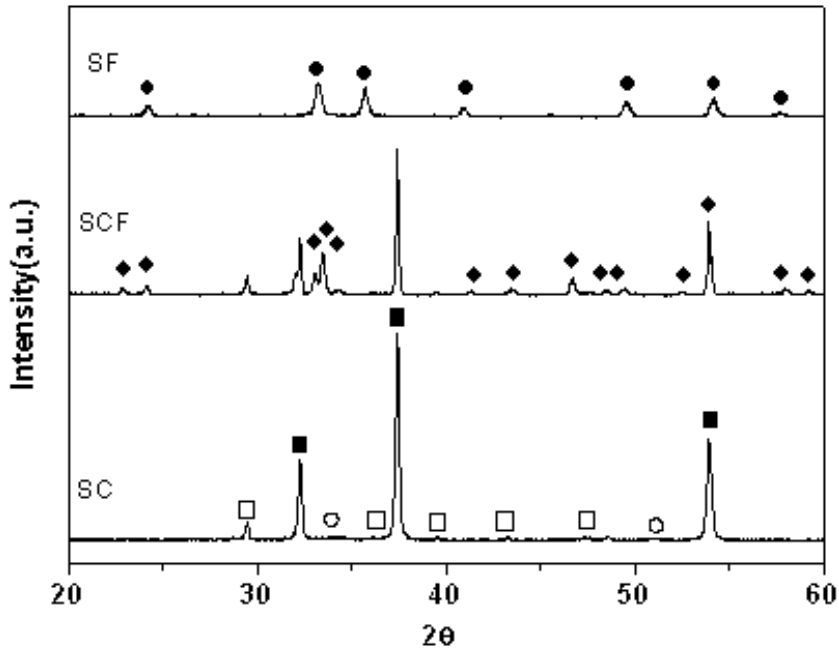

Fig. 6 XRD patterns of different oxides after reaction at 300 °C for 30 min (■) CaO, (●) α-Fe_2O_3, (○) $Ca(OH)_2$, (♦) $Ca_2Fe_2O_5$, (□) $CaCO_3$

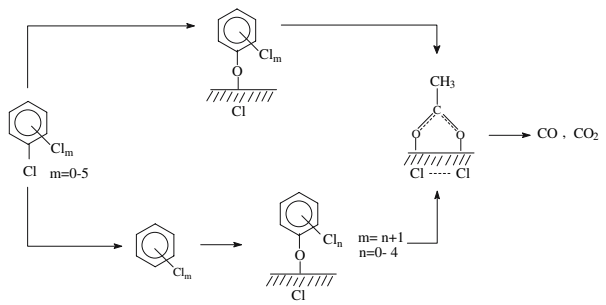

Fig. 7 A proposed reaction mechanism for the decomposition of HCB over SCF

presence of several partial oxidation products (i.e., phenolate and acetate) on the surface of the oxides examined. The products after reaction have been analysed by XRD and chloride selective electrode. Ca–Fe composite oxide exhibited the highest extent of mineralization for organic chlorine among the different oxides tested. The best catalytic activity of Ca–Fe composite oxide may be related to the surface acidity accompanied with the formation of $Ca_2Fe_2O_5$. Combined with the previous research results of HCB decomposition, the following conclusion can be drawn: two types of competitive reactions were identified and shown to take place simultaneously during HCB decomposition. (1) hydrodechlorination results in the formation of lower chlorinated benzenes and (2) oxidation of aromatic rings leads to the breaking of aromatic ring and the formation of oxidation products. The oxidative degradation was the major process when HCB was decomposed.

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