Mechanochemical decomposition of pentachlorophenol by ball milling

WEI Yinglei, YAN Jianhua, LU Shengyong*, LI Xiaodong

State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China. E-mail: lushy@zju.edu.cn

Received 17 January 2009; revised 02 April 2009; accepted 23 July 2009

Abstract

The mechanochemical dechlorination of pentachlorophenol (PCP) was studied using CaO and SiO$_2$ powder as additives. The effects of the milling time and additives on the dechlorination rate were investigated. The resulting product was characterized by X-ray diffraction (XRD), Fourier transform infrared spectra (FT-IR), thermogravimetric analysis (TG) and ion chromatography (IC). It is found that grinding operation could dechlorinate PCP, with the formation of inorganic chloride and amorphous carbon. The addition of quartz to the grinding mixture facilitated dechlorination. On the basis of the experimental results, the decomposition mechanism was proposed. Decomposition predominantly proceeds through rupture of C–Cl bond in PCP molecule, followed by the formation of inorganic chlorides.

Key words: ball milling; dechlorination; mechanochemical; pentachlorophenol

DOI: 10.1016/S1001-0742(08)62485-7

Introduction

Pentachlorophenol was widely used as wood preservative, pesticides and bactericide in China, and more recently has received increased attention due to its high toxicity and long persistence. Traditional oxidative treatment, such as incineration in waste combustors, represents a significant environmental hazard, since it can lead to even worse compounds, such as polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF). Therefore, new, reasonable and safer PCP disposal methods are needed urgently.

In recent years, the mechanochemical (MC) method has been applied in the environmental field. Numerous organochlorine compounds, such as DDT (Rowlands et al., 1994), PVC (Mio et al., 2002; Sakei et al., 2001; Tongamp et al., 2007; Xiao et al., 2008), PCB and PCDD/Fs (Monagheddu et al., 1999; Birke et al., 2006), have been successfully degraded by MC treatment. In these studies, MC treatment of organochlorine compounds is investigated because it is a noncombustion technology that requires no heating or off-gas treatment and does not generate secondary pollution.

Birke et al. (2006) verified that PCP can be rapidly and entirely dechlorinated by ball milling with magnesium and amine: after grinding for 30 min, PCP was entirely changed into phenols; however, there is little information about reaction mechanism and influential factors.

Thus, the present article consists of two parts. In the first part, the dechlorinated products of PCP were characterized, to provide information about their structure, mechanisms of dechlorination and possible reaction. In the second part, four comparative tests on MC treatment of PCP were conducted to investigate the feasibility of MC treatment of PCP at relatively low rotating speed. This article provides some basic information on MC degradation of PCP by co-grinding with some additives.

1 Materials and methods

1.1 Materials

The PCP sample was chemical reagent quality (purity > 98.5%) (Qinpu Chemical Co., Ltd., Shanghai, China). Two types of additives were prepared: CaO only; and a mixture of CaO and SiO$_2$. CaO and SiO$_2$ were heated at 1027 K for 3 h. The composition of the sample mixtures are: (1) 19.2 wt.% PCP and 80.8 wt.% CaO; (2) 13.7 wt.% PCP, 57.7 wt.% CaO and 28.6 wt.% SiO$_2$. In these mixtures, the molar ratio of Ca to Cl in the sample mixtures was 4, and the total weight of the sample in the milling pot was kept constant at 7.0 g.

1.2 Experimental procedure

A planetary ball mill (XQM-0.4L, Kexi, China) was used for the MC treatment of the PCP with additives mixture. A schematic representation is shown in Fig. 1.

Four tests were conducted. For each test, 7.0 g sample mixture was put in the milling pot, adding a certain quantity of milling balls of different sizes, and then subjected to grinding at 400 r/min under dry atmospheric conditions for various time periods. Detail parameters for each test are shown in Table 1. To prevent over heating, the milling was...
stopped for 30 min after every 30 min grinding operation.

1.3 Characterizations

The ground mixture was characterized using the following analytical methods: X-ray diffraction (XRD) analysis, conducted by using a diffractometer (D/max-3B, Ragu-kaku, Japan) with Cu-Kα radiation to identify the phase formed after grinding; infrared spectra of the ground samples, measured using a Fourier transform infrared (FT-IR) spectrometer (Thermo Nicolet NEXUS 670) with the KBr disk method; thermogravimetric analysis (TG) (TGA/SDTA851e, Mettler-Toledo, Switzerland), conducted at a heating rate of 30 K/min from 273 to 1027 K in N2.

The ground samples were further treated as follows: 0.1 g milled sample was dispersed in 1–2 mL of 7% nitric acid for 2 h, then the suspension was filtered and washed with ultra-pure water to remove inorganic chlorine in the samples. Chlorine ion in the filtrate was analyzed by ion chromatography (IC) (729 Basic IC, Switzerland). Samples of 0.2 g was extracted by 200 mL hexane for 2 h using an ultrasonator. The extract was analyzed by GC/MS (CP-3800/1200L, Varian, USA) with a 30-m DB-5 quartz capillary column to measure the residual PCP content and identify the products in the ground sample. The temperature program for GC oven was: initial temperature 80°C, held for 2 min; 80–200°C at 25°C/min; 200–280°C at 5°C/min, held for 20 min. Carrier gas: helium (99.999%), 1.2 mL/min; 1 µL of the extract was injected in splitless mode. Mass spectrum condition: ion source temperature 280°C; the mass spectrometer was operated at 70 eV ionization energy.

2 Results and discussion

2.1 Decomposition mechanisms of PCP

2.1.1 Decomposition of PCP as a function of time

Figure 2a shows that residual PCP in the ground samples of Test I and Test II decreases rapidly, as a function of grinding time. Only about 18.7% (Test I) and 6.6% (Test II) of the initial PCP were still left in the samples ground for 1 h. However, the yield of chlorine ion did not increase so rapidly for several hours. After 6 h grinding, the residual PCP were both less than 1%, indicating that the mechanochemical degradation of PCP was very effective. The yield of chlorine ion reaches 99.9% of total chlorine when the sample was ground for more than 8 h.

Figure 2 shows residual PCP and the yield of chlorine ion in the ground samples of III and Test IV. Only about 1.6% of the initial PCP was still left in the sample IV.

<table>
<thead>
<tr>
<th>Table 1 Parameters for each test</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PCP</strong></td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>Test I</td>
</tr>
<tr>
<td>Test II</td>
</tr>
<tr>
<td>Test III</td>
</tr>
<tr>
<td>Test IV</td>
</tr>
</tbody>
</table>

* Molar ratio of Ca to Cl in PCP is 4; “/”: none.
after 1 h, and the yield of chlorine ion reached 99.9% when the sample was ground for more than 5 h. Compared with the high efficiency of Test IV, the mechanochemical degradation of PCP in Test III occurred not so effectively: after 5 h grinding, less than 5% of original PCP was left, and the yield of chlorine ion only reached 72.3% of total chlorine within 10 h grinding.

The results obtained clearly indicate that PCP decomposes through a mechanochemical reaction and the chlorine transforms from aromatic chlorides into inorganic chlorides. The most likely explanation for the lower yield of chlorine ion at the initial stages of the reaction is as follows: the rupture of C–Cl bonds in PCP occurs at the initial reaction stage, forming partly dechlorinated products, i.e., trichlorophenol, tetrachlorophenol and tetrachlorobenzene. Among these substances, chlorine subsists as aromatic chlorides. Hence, the yield of chlorine ion is lower at the initial reaction stages. When grinding continues, all C–Cl bonds are cut off, and aromatic chlorine is transformed into inorganic chlorine. Besides, since grinding is conducted in air and the pot is not completely sealed, traces may escape into environment during experiment (e.g., while removing the samples from the mill pot).

In order to confirm our hypothesis, further investigation and identification of the compounds and gases formed was taken into consideration.

2.1.2 Organic products after decomposition

The products extracted from the mixture samples of Test I–IV were identified by GC/MS analysis (Fig. 3). A strong peak corresponding to the original PCP (E, 24.670 min) was observed. Small peaks corresponding to trichlorophenol (A, 19.826 min; B, 20.646 min; isomers have different retention time), tetrachlorophenol (C, 22.651 min) and tetrachlorobenzene (D, 23.944 min) were also observed. And the peak assigned to C₁₆H₂₂O₄ (F, 27.371 min) can be observed, indicating fatty acid compound is gradually formed. In the spectrum of sample II which corresponding to the addition of SiO₂, new peaks due to cyclohexasiloxane (I, 15.603 min), cyclopentasiloxane (H, 17.490 min) and dichlorophenol (G, 18.740 min) were also observed. It will be discussed in detail in Section 2.2. Considering that some products formed may not dissolve in hexane, different solvents such as acetone and toluene were also used to extract the ground samples. However, no other new intermediate phases can be found.

The high-electronegativity of chlorine atom in chlorophenols make it more difficult to be decomposed than phenol. Charge transfer occurs by high-energy collision on CaO, hydrogen radicals (H·) are induced, and nucleophilic substitution reactions occur for chlorophenols. Cl-atom splits off from chlorophenol to form chlorine ion and aromatic intermediate without Cl.

Fig. 3 GC/MS spectra of the hexane extracts from samples milled for 0.5 h.
Then ring-opening reactions take place. Dechlorination of chlorinated phenols occurs through the pathway which is determined by the number and position of Cl-substituents. In our test, PCP is dechlorinated to TeCP at first and then to TCP etc., as Fig. 3 illustrates.

2.1.3 XRD patterns of the mixture products

Figure 4 shows XRD patterns of the mixtures of Test I and Test II ground for different periods of time. XRD patterns of the sample III and IV ground after 10 h are also showed in Fig. 4. Since SiO$_2$ was not used in Test I, the peaks corresponding to SiO$_2$ are not seen in Test I. And the peak intensity of SiO$_2$ in other patterns remains basically unchanged. Although SiO$_2$ may participate in MC reactions, the peak intensity of SiO$_2$ does not change because excess in amount was used. In all figures, the peak intensity of CaO in the pattern decreases with the MC treatment progressed. This suggests that CaO in the mixture was gradually consumed during the MC treatment. Peaks corresponding to Ca(OH)$_2$ are found in the patterns, this is due to the hydration of CaO by moisture in the air. In the spectra of Test I and Test II, no new peak was observed in 1 and 10 h ground samples, suggesting that any other reaction products formed are amorphous. The mechnochemical decomposition of PCP proceeded through a dechlorination pathway, forming intermediate compounds calcium hydroxide chloride (CaOHCl). However, the formation of a crystalline phase of Ca(OH)Cl cannot been observed from the XRD analysis, suggesting that the chloride formed is amorphous (Tanaka et al., 2003). After 10 h grinding, the peak of carbon is observed except Test III. The peak intensity of C increases with time. Some weak Ca-carbonate peaks are found by XRD in Test II. It is suggested that oxygen removed from CaO tends to connect with C to form organic C–O bond. This component combines with excess CaO sample in the product, leading to the formation of CaCO$_3$ (Tanaka et al., 2003). However, the peak intensity of CaCO$_3$ decreased with grinding time, contrary to the result of Tanaka et al. (2003a). The reason for this is that CaCO$_3$ itself can be used as an additive on dechlorination of chlorinated organics by MC treatment. When CaCO$_3$ is used as an additive, it caused a decarboxylation reaction (Sakei et al., 2001).

According to the results and discussion above, it is proposed that the summary reaction between CaO and PCP during the grinding can be expressed as:

$$C_6OHC_5 + CaO \rightarrow C + CaCl_2 \cdot nH_2O$$  (1)

When a C–Cl bond is cut off, Cl tends to combine with CaO. On the other hand, the O of CaO is inclined to combine with PCP via hydrogen bonding. The exchange results in Ca chloride and an organic phase, consisting of C, H and O. The latter tends to dehydrate during grinding, while Ca-chloride has a strong tendency to absorb water. As a result, hydrated Ca-chloride and amorphous carbon are obtained as the most stable state through water exchange (Tanaka et al., 2003).

2.1.4 TG curve of the mixture products

Figure 5 shows TG-curves of the pure PCP sample and the products of Test I, ground for different periods of time. TG-curves of Test I–IV were approximately the same, thus take the TG curve of Test I for example. In the case of original PCP, three weight loss regions were observed: a significant weight loss in the region of 140–230°C, which attributed to the volatilization of PCP. The residual weight was about 16%. A second weight loss of about 7% is observed in the temperature range 230–430°C. The rate of weight loss was much lower, compared with the
first region. In this region, PCP pyrolysis occurred, with formation of involatile products. In temperatures ranging 430–480°C, the rate of weight loss increased. This suggests that the involatile products volatilize because of the higher temperature. At temperature as high as 480°C, no weight loss was observed. Unlike the original PCP sample, a continuous weight loss occurred in the curves of the ground samples, starting at 50°C, which can be attributed to the volatilization of moisture and unknown organic products. The weight loss due to the PCP volatilization has disappeared, indicating that PCP is gradually decomposed by the MC reaction with increase in grinding time. This assumption is supported by the GC/MS results of residual PCP concentration: only 1% of the original PCP was left in the samples ground for 5 h or more, so no significant weight loss can be observed in the TGA-curves. The first significant weight loss due to the volatilization and thermal decomposition of the products formed by grinding, can be observed in a temperature range of 400–460°C. Weight loss values of samples ground for 1, 5, and 10 h were measured to be 10.42%, 9.63%, and 3.61%, respectively. Other significant weight loss can be observed around the temperature of 600–700°C, owing to the pyrolysis of inorganic carbon, formed after grinding. In the temperature of 400–460°C and 600–700°C, the longer the grinding time, the less the ground sample weight loss will be. This indicates that the amount of organic compositions in samples after grinding become smaller and they behave more like inorganic ones rather than tending to burn out (Tanaka et al., 2003c). Comparing the TG curves of ground samples for different periods of time, the longer grinding time is, the less organic compounds existed in ground samples.

2.1.5 FT-IR monitoring of the ground samples

Figure 6 shows FT-IR spectra of the ground samples of Test I for different periods of time together with that of the pure PCP sample. FT-IR spectra of Test I–IV were approximately same. Therefore, only spectra of Test I is displayed. Peaks around 700 cm\(^{-1}\) appear in the spectrum of pure PCP sample due to C–Cl stretching vibration, and these peaks still can be observed in the spectra of the ground samples after 1 and 5 h. The intensity of the peaks decreases gradually with increase in grinding time, and disappears in spectra of samples ground for 10 h. It indicates that all the C–Cl bond in PCP has been cut off, all the chlorine in PCP structure have been removed. Peaks appear in the pure PCP sample at around 1400 cm\(^{-1}\), which are attributed to benzene ring mode. The intensity of the peaks also decreases as grinding progresses from 1 to 10 h, indicating that benzene ring has been gradually broken. New peaks due to the C–O bonding are observed in the spectra of the ground samples at around 1500 cm\(^{-1}\), suggesting the existence of CaCO\(_3\) in the product. This result is consistent with the XRD analysis shown in Fig. 4. It is particularly worth noting that in case of the pure PCP sample, there is only one peak at 770 cm\(^{-1}\) is observed. This peak can be assigned as out-of-plane bending vibration of a benzene ring which has five adjacent H atoms substituted (γ\(_{\Phi,3}\)). In contrast to the pure PCP, another peak at around 800 cm\(^{-1}\) is observed in the spectra of ground samples in addition with the peak around 770 cm\(^{-1}\). The new peak corresponds to out-of-plane bending vibration of a benzene ring, which has three adjacent H atoms substituted (γ\(_{\Phi,4}\)). These findings prove that dechlorination occurred during the process of MC treatment of PCP, i.e., C–Cl bond has been cut off, formed TCP or other compounds whose benzene ring has three adjacent H atoms substituted.

2.1.6 Decomposition mechanism discussion

From the products analysis (Section 2.1.1–2.1.5), it is derived that free radicals were induced by grinding on CaO surfaces and subsequently the charge transfer occurred on the organic PCP. C–Cl bonding in PCP tended to be cut.
off to produce some intermediates or products. Cl atom split off from the C–Cl bond of PCP. At the same time, CaO reacted with the Cl atom to form Ca(OH)Cl intermediate. Cl substituents on PCP have been gradually removed from the structure of a benzene ring. PCP can be dechlorinated following the pathways of dechlorination and oxidation. Fatty acid compounds (i.e., C_{16}H_{22}O_{4}) were formed through oxidation reaction. With a series of complicated reactions induces, a mixture of CaCl_2·nH_2O and amorphous carbon are formed as the final products.

2.2 Effect of SiO_2 as an assistant additive in the mechanochemical reaction

Test I and Test II were performed to provide better insight into the effect of SiO_2 as assistant additive in the mechanochemical reaction. All other experiment parameters were the same. The degradation extent of PCP can be followed directly from the sample color: with increasing grinding time the color of the starting powders changes from white to black gradually, indicating that “free carbon” has been formed. For the same grinding time periods, these sample colors of Test II were always darker than those of Test I. As shown in Fig. 7, after grinding for 15 h, Test II sample is deep black, while sample of Test I is gray. It is indicated that more free carbon was formed in sample II than in sample I, and PCP decomposes more efficiently while being ground with the aid of quartz. The results of the residual PCP concentration analyzed by GC/MS and chlorine ion concentration analyzed by IC corroborate our analysis. After grinding for the same time periods, residual PCP in the ground samples I was more than that of sample II, and PCP decomposes more efficiently while being ground with the aid of quartz. The results of the residual PCP concentration analyzed by GC/MS and chlorine ion concentration analyzed by IC corroborate our analysis. After grinding for the same time periods, residual PCP in the ground samples I was more than that of sample II, and the yield of chlorine ion for Test I was less than that for Test II, as shown in Fig. 2. The yield of chlorine ion of Test I reaches 99.9% after 8 h. And for Test II, it only needs 6 h.

The organic intermediates of Test I and Test II formed after grinding 0.5 h are compared in Fig. 3. The results of the organic intermediates analyzed by GC/MS also corroborate our analysis above. After grinding for the same time periods, the peaks intensity of A–D in Test II is more than those of Test I, indicating that more intermediates have been formed in Test II. In addition, new peaks of cyclohexasiloxane (I, 15.603 min), cyclopentasiloxane (H, 17.490 min) and dichlorophenol (G, 18.740 min) were identified in Test II. The formation of dichlorophenol indicates that dechlorination of PCP occurred more deeply in Test II. The formation of cyclohexasiloxane and cyclopentasiloxane is because of the crosslink of PCP and SiO_2.

The XRD analysis shows how inorganic compounds changed during the grinding process. As shown in Fig. 4 of Test II, the peak intensity of SiO_2 remained basically unchanged for all periods of time because excess in amount is used. The peak of carbon increases with time, both in Test I and Test II. It indicates that carbon has been formed as one of the final products in these two tests. But the quantification of carbon in mixture is difficult now. It will be further investigated in the future.

The results above demonstrate that SiO_2 tends to accelerate the mechanochemical process, as noted by Zhang et al. (2001). SiO_2 acts as an assistant additive. The might explanations are: (1) the addition of quartz to the grinding mixture increases the contacting areas of PCP and CaO, more impact energy will be accumulated, the collision probability of PCP molecule will be increased and therefore accelerates the decomposing reaction; (2) the addition of quartz to the grinding mixture changed the energy distribution of PCP molecule. O-atom in SiO_2 tends to combine with PCP via hydrogen bonding. The exchange results in changes in bond-energy of PCP. Therefore, the dechlorination of PCP occurs more easily.

2.3 Effect of milling material in the mechanochemical reaction

Test III and Test IV were performed to investigate the effect of milling material on PCP degradation under the same grinding conditions. Al_2O_3 milling balls were used in Test III, while stainless steel milling balls were used in Test IV, in both cases with an Al_2O_3 milling pot. Considering that the density of stainless steel milling balls is denser than Al_2O_3 ones, part of the stainless steel milling balls was taken out to avoid the risk of coming out of balance during ball milling at very high speed. Again, the degradation rate of PCP was monitored by means of the
sample color change. The white color remains basically unchanged during the entire Test III. During Test IV the sample ground for 3 h turned deep black, suggesting that free carbon has been formed in the ground products.

On the basis of the analytical GC/MS-results for the residual PCP concentration and chlorine ion concentration analyzed by IC, the residual PCP in ground samples III was always more than for sample IV, after grinding for the same periods of time (Fig. 2). And the yields of chlorine ion in ground sample III were always far below sample IV. Although free carbon was not formed after grinding 10 h in Test III, the residual concentrations of PCP were quite low. This is mainly because the specific impact energy caused by the collision between two Al$_2$O$_3$ balls or the ball-wall interface can cut off the C–Cl bond, but it was not large enough for rupturing covalent C–C bond. Therefore, free carbon cannot be observed in ground sample III. The products formed in sample III were partly dechlorinated products, i.e., trichlorophenol (TCP), tetrachlorophenol (TeCP) and tetrachlorobenzene according to dechlorination pathway. They were identified by GC/MS analysis in Fig. 3. After grinding for the same time periods, the peak intensity of PCP (E) in Test IV is less than those of Test III, and the peak intensity of intermediates (i.e., C, I, H, F) in Test IV is more than those of III, indicating that more PCP have been decomposed and more intermediates have been formed in Test IV.

Again, the inorganic products formed after 10 h grinding in sample III and IV were monitored by means of the XRD analysis. As shown in Fig. 4, the peak of carbon has been observed in sample IV, but it can not be seen in sample III. This corroborates our analysis that carbon has not been formed as one of the final products in Test III. But the quantification of carbon in mixture is difficult now. It will be further investigated in the future. And the peaks corresponding to Al$_2$O$_3$ are found in the pattern of sample III; it is due to the Al$_2$O$_3$ milling ball used in test. Al$_2$O$_3$ powder may split away from the Al$_2$O$_3$ milling ball.

The results above demonstrate that PCP decomposes more completely during MC treatment by ball milling when using stainless steel materials. This can be explained as follows: (1) Mio et al. (2002) found that the dechlorination rate of PVC is proportional to the specific normal impact energy of the balls. The specific impact energy $E_w$ can be calculated by equation:

$$E_w = \sum_{j=1}^{n} \frac{1}{2W} m V_j^2$$  \hspace{1cm} (2)

where, $V_j$ denotes the relative velocity between two colliding balls or a ball colliding against the mill wall, $m$ is the mass of the grinding media, $n$ is the number of collisions per second, and $W$ is the weight of sample charged into the mill pot. Thus, $E_w$ increases with an increase in both $m$ and $V_j$ and with a decrease in $W$. The mass of a stainless steel ball is obviously higher than that of Al$_2$O$_3$ ball with the same volume, thus the specific impact energy of stainless steel materials is greater. Therefore, the degradation of PCP using stainless steel materials is faster than using Al$_2$O$_3$ materials. (2) According to the theory proposed by Lamparski et al. (1994) and Loiselle et al. (1997), a large amount of excessive energy is accumulated in a solid surface subjected to intensive milling in the form of structural defects and an extended network of intergranular boundaries. These defects exert a strong influence on the migration of the reactant in the stressed lattice surface. With continued milling, the specific surface area increases, local states develop, and intermixing is forced to a molecular level. Chemically active non-equilibrium states are formed, and the intensification of the interdiffusion process facilitates the breakup of chemical bonds. Plasma region is formed due to high-energy electrons and plasmas excitation both occur in the chemically active non-equilibrium states. Electron energy induced by plasma region under high energy excitation may be over 10 eV. Generally speaking, electron energy induced by thermal chemical reaction above 1000°C is generally only 4 eV and no more than 6 eV, even by photolysis induced by means of UV radiation. Besides, discharge may happen on the surface of metal ball during high speed collision. Thus high-energy electrons and plasmas are more easily induced to form Plasma Region. As a result, the degradation of PCP using stainless steel materials is better than adopting ceramic materials.

3 Conclusions

PCP samples were mixed with CaO-powders using SiO$_2$ as an assistant additive. The mixtures were subjected to grinding in air using a planetary ball mill to investigate MC to degradation PCP sample. Two kinds of milling tool materials were used: alumina and stainless steel. Dechlorination products of PCP were characterized by means of XRD, FT-IR, TG and IC. The results are summarized as follows:

(1) The MC method is very effective for decomposing PCP. When using stainless steel balls, only 1.6% of the initial PCP was detected in a sample IV ground for 1 h. Thus, the MC treatment is very effective for treatment of PCP, with a simple process and wide prospects for industrial application.

(2) The PCP decomposition pathway by MC treatment is suggested as follows: when a C–Cl bond is cut off, Cl tends to combine with CaO, and a complicated series of reactions is induced; finally a mixture of CaCl$_2$·nH$_2$O and amorphous carbon is formed as final products.

(3) The addition of SiO$_2$ and using stainless steel materials will help to improve the MC reaction.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 50776081), the Doctoral Program of Higher Education (No. 20060335129) and the Project on Science and Technology of Zhejiang Province of China (No. 2008C23090).

References


