Color-masked and nano-size catalysts embedded in polymers for reducing dioxin emission

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Abstract

Instead of removing dioxin by the end-of-pipe technologies, there is an attempt currently to reduce the dioxin emission during the incineration of waste. In this concept, dioxin suppressing catalysts are pre-mixed in polymer materials during the manufacturing stage. During the calcinations of the wastes, the catalysts in the polymer can prevent from the formation of dioxin.

In this work, we have attempted to prepare polymer embedded catalysts for dioxin decomposition. Especially, nano-sized and color-masked Fe/Ti catalysts have pale or white color and showed better activity comparing individual Fe or TiO_2, and these materials were embedded inside polymer. During incineration of catalyst–embedded polymer, most of noxious gas was successfully removed. We can also control properties such as transmittance, tensile strength, etc. by changing catalytic materials embedded inside polymer.

Keywords: dioxin, Fe-based catalysts, color-masked catalysts, functional polymer, incineration

1 INTRODUCTION

Dioxin is released from stationary or mobile sources. Thermal waste incinerators are the most typical example among stationary sources. The flue gas from incinerator is composed of SO_x, NO_x, particulate matter, chlorinated volatile organic compounds (VOCs), etc.. Especially, polychlorinated dibenzodioxins(PCDDs) and dibenzofurans (PCDFs), so called dioxins, well known as a carcinogenic material is included that flue gas [1-2]. So many countries in the world have regulated those materials [3-5] due to their toxicities.

Many research groups have focused on catalytic decomposition of dioxin with end-of-pipe converter of incineration system. There are many catalysts for dioxin decomposition. Noble metals such as Pt, Pd and Ir were reported catalysts for dioxin decomposition [6-7]. But, since they are very expensive, several transition metal oxides such as CrO_x, V_2O_5-WO_3 have been reported catalysts for dioxin removal. However, CrO_x [8] and V_2O_5-WO_3 [9] based catalysts could act as toxic materials and pollutants themselves. Fe-based catalysts have alternated transition metal-based catalysts due to their environmental safety.

Instead of removing dioxin by the end-of-pipe technologies, there is an attempt currently to reduce the dioxin emission during the incineration of waste. In this concept, dioxin suppressing catalysts are pre-mixed in polymer materials during the manufacturing stage. During the incinerations of the wastes, the catalysts in the polymer can prevent form the formation of dioxin. For practical purpose, one may consider criterions when they produce the catalyst/polymer composites: these catalysts should be colorless for dyeing, highly active for dioxin decomposition and the catalyst particles are very small for homogeneous dispersion in the polymer. It was reported that nano-sized particles of α-FeOOH dispersed in polyethylene were active for reducing dioxin, but its brown color limited its usage [10].

In this work, bulk Fe-based catalysts are coated with white nano particles by zeta potential difference and Fe precursor are impregnated on pore of white nano particles in order to mask color and keep on small size. Therefore, our goals are to synthesize functional polymer embedded catalysts for dioxin decomposition and to remove dioxin and other pollutants during incineration of these polymers.

2 EXPERIMENTAL

2.1 Preparation of nano-sized Fe_3O_4 catalysts

It is important to prepare Fe_3O_4 nano particles in an aqueous solution with a molar ratio of Fe(Ⅱ)/Fe(Ⅲ) = 0.5. 10.285mL of 1N HCl and 25mL of purified, deoxygenated water were mixed. 8.65g of $FeCl_3$ $6H_2O$ and 3.18g of $FeCl_2$ $4H_2O$ were dissolved in the solution with vigorous stirring. The mother solution was dropped into 250mL of 1.5M NaOH solution under vigorous stirring. Generated precipitate was repeated centrifuging at 4000rpms and washing with purified deoxygenated water [11] until precipitate and water were not separated. The last step,

particles were filtered by ultra filtration membrane (pore size 25nm) and dried at room temperature.

2.2 Preparation of color-masked catalysts

Prepared nano-sized Fe_3O_4 particles were coated by nano-sized TiO_2 using zeta potential difference under conditions of pH 6 and TiO_2/ Fe_3O_4 weight ratio 19/1.

Nano-sized FeO_x/TiO_2 catalysts were prepared by incipient wetness method. $FeCl_3$ $6H_2O$ acted as precursor and nano-sized TiO_2 (HOMBIKAT UV100, 100nm) was used as support. 5wt.% and 10wt.% Fe was impregnated on support. After impregnation, the catalyst was dried at 100℃ for 12hrs and then calcined at 500℃ for 5hrs.

2.3 Activity tests of catalysts

In order to test activity of the catalysts in a packed-bed reactor, we utilized 1,2-dichlorobenzene (*o*-DCB) instead of dioxin having similar structure and toxicity under reaction conditions of inlet concentration of 1,000ppm, weight hourly space velocity (WHSV) of 6,000 L/kg-cat/hr, and temperature of 473-973K.

2.4 Preparation of functional polymer

1wt.%, 5wt.% and 10wt.% of prepared catalysts were added into Poly Ethylene (PE) by electrically heated measuring mixer (Brabender). Procedure was like these.

① Heat the mixer to 200℃ and keep on.
② Put PE chips and catalysts
③ Mix PE and catalysts by Brabender for 7min.
④ Clean the mixer with PE until screw become clear.

In order to test tensile strength and transmittance, small film was prepared by MiniMax molder.

2.5 polymer incineration tests

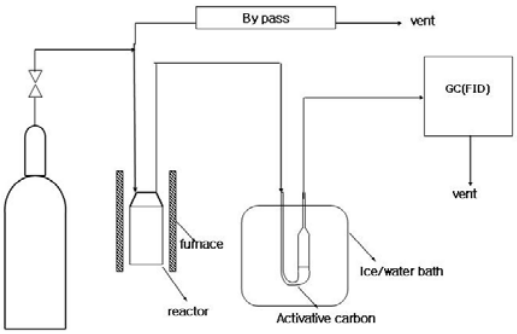


Figure 1: Apparatus for polymer incineration

Apparatus for incineration tests of polymer and functional polymer is shown in Figure 1. The flow rate of carrier gas was 100cc/min. Polymer was incinerated at 400℃. The noxious gases adsorbed on activated carbon at 0℃. And then gases desorbed from activated carbon at 400℃.

3 RESULTS AND DISCUSSION

3.1 Fe-based catalysts

Nano-sized Fe_3O_4 catalysts had black color and magnetic property. XRD pattern of Fe_3O_4 was shown in Figure 2. The size of particle was about 30nm by Scherrer equation. (Inverse triangle means typical peaks of Fe_3O_4)

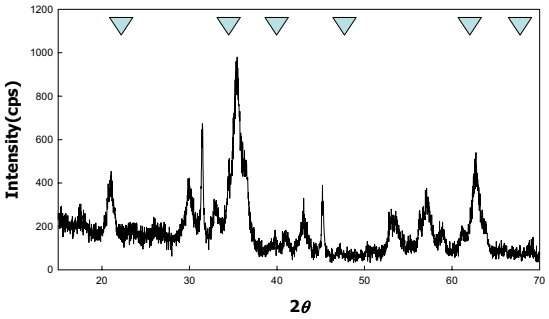


Figure 2: XRD pattern of Fe_3O_4 nano particles.

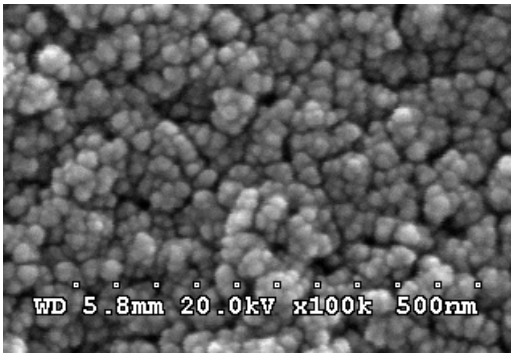


Figure 3: The SEM image of Fe_3O_4 particles.

Figure 3 shows the SEM image of the Fe_3O_4 particles. The shape of Fe_3O_4 was spherical and we could confirm its size was around 30nm. Zeta potential of Fe_3O_4 and TiO_2 particles are shown in Figure 4. Surface charge of Fe_3O_4 and TiO_2 are (+) and (-) respectively around pH 6. We, therefore, could obtain the optimal condition of zeta potential coating was pH 6.

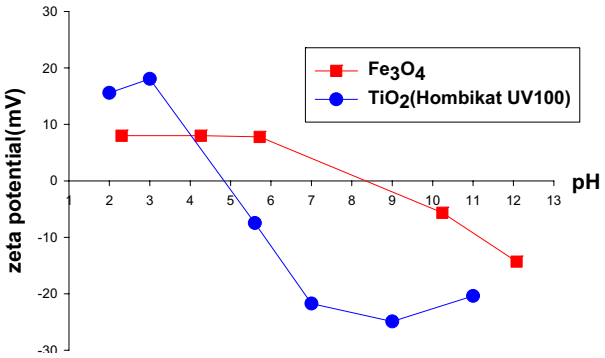


Figure 4: Zeta potential of particles.

3.2 Activity tests of catalysts

We tested activity of catalysts through *o*-DCB oxidation. As shown in Figure 5, Fe-based catalysts had conversion above 95% at about 500℃. Especially, FeO_x/ TiO_2 and TiO_2 coated Fe_3O_4 (Ti/Fe) catalysts have shown more active for *o*-DCB oxidation than bulk Fe_3O_4 due to Ti/Fe synergistic effect. In case of bulk Fe_3O_4, as temperature increases, crystal grows up and area of active site decreases. Since Fe-based catalysts are very cheap and eco-friendly, they can be used as alternative of V-based oxidation catalysts. Moreover, since their size is below 200nm and their color is pale or white, they can be applied to synthesize functional polymer.

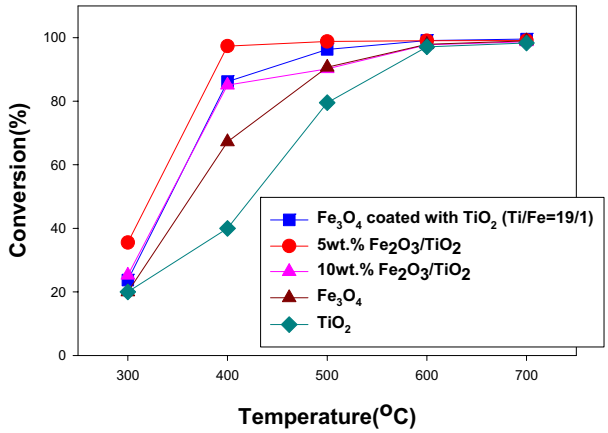


Figure 5: Activity test of catalysts by *o*-DCB oxidation.

3.3 Properties of functional polymer

PE embedded Fe_3O_4 and Ti/Fe particles were prepared and the weight ratio of particle/PE was 1/99. The transmittance of PE embedded Ti/Fe catalysts is better than in case of Fe_3O_4 particles as shown in Figure 6. As particles were added into polymer, the modulus increased. In case of blank PE, the inflection point was shown near 105℃. That point is not T_g. Commercial polymers have individual thermal history according to synthesis condition and that point is just caused by thermal history. Generally, the glass transition temperature (T_g) of polymer embedded inorganic particles increase because inorganic particles raise crystallinity between polymer chains. However T_g of PE embedded Ti/Fe particles is similar regardless of additive as shown in Figure 7. In other words, polymeric property is almost never affected by Ti/Fe catalysts. Therefore, functional polymer embedded Ti/Fe catalysts will use instead of blank PE in various applications and we will be control mechanical property according to changing amount of catalysts. So we will synthesize functional polymer with various specification according to our intention.

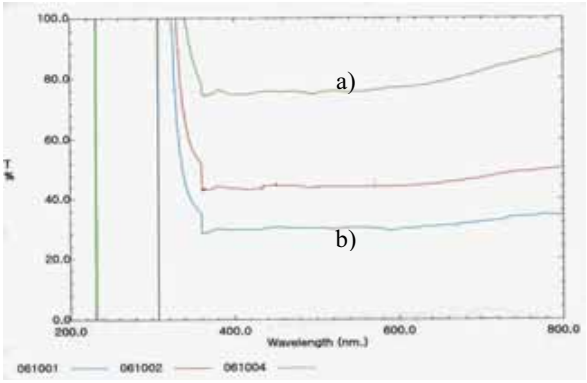


Figure 6: The transmittance comparison.
a) PE embedded Ti/Fe particles
b) PE embedded Fe_3O_4 particles

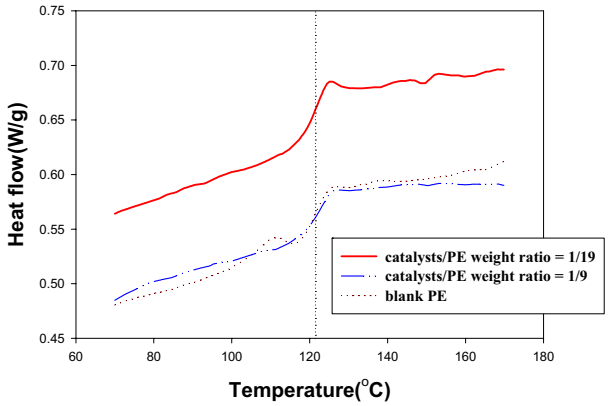
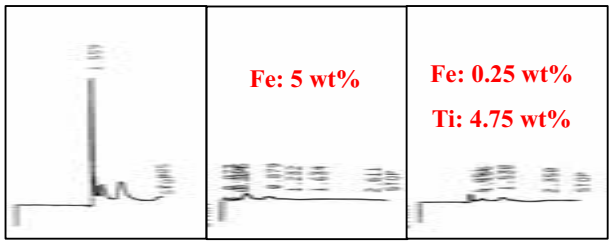


Figure 7: The glass transition temperature of polymer.

We could see that noxious gases were removed by catalysts during polymer incineration as shown in Figure 8. In case of blank PE, hydrocarbons from desorbed gases were detected. However, in case of PE embedded catalysts, hydrocarbons were removed. Especially, in case of PE embedded Ti/Fe particles, noxious hydrocarbons were almost removed.



PE Fe_3O_4 +PE Ti/Fe + PE

Figure 8: Polymer incineration test.

4 CONCLUSIONS

According to above discussion, Ti/Fe particles have better activity for *o*-DCB oxidation than bulk Fe-based particles. Fe-based catalysts are less harmful than other transition metal-based catalysts and have similar activity above 400℃. Moreover, Ti/Fe catalysts can be used as catalysts for synthesis of functional polymer embedded catalysts for dioxin removal during incineration. We have prepared PE embedded 1wt.%, 5wt% and 10wt.% of Ti/Fe particles. According to amount of particles, properties of PE were varied. However, T_g almost never changes regardless of additives. That is, polymeric property difference between blank PE and functional PE is negligible. So, functional PE can be used as alternative of PE. Through the incineration test, functional polymer embedded catalysts generate less noxious gases than blank polymer during incineration. Therefore functional polymer reduces chance for formation of dioxin.

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