

## [Letter]

## Development of Chlorine Tolerant Degradation Catalyst for Chemical Recycling of Polyethylene

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Catalytic degradation of low density polyethylene (LDPE) including small amounts of poly(vinyl chloride) (PVC) has been carried out to develop a chlorine tolerant catalyst for chemical recycling of waste plastics. H-galloaluminosilicate has been found to be highly active as a catalyst for converting LDPE into aromatic hydrocarbons in the presence of hydrogen chloride.

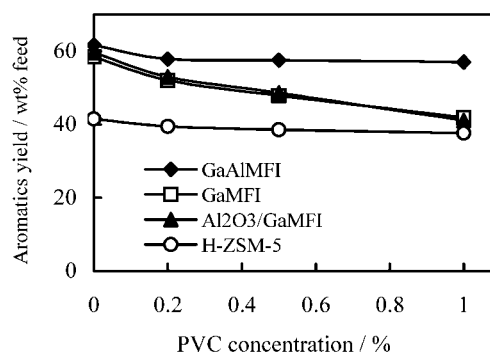
**Keywords:** Low density polyethylene, Chemical recycling, Chlorine tolerance, Galloaluminosilicate catalyst, Catalytic degradation, Poly(vinyl chloride)

The development of a technology for converting waste plastics into feedstock is growing in importance in an effort to conserve limited natural resources and to protect the environment. Recently, it has become possible to convert polyolefins into aromatic hydrocarbons, including benzene, toluene and xylenes (BTX) with high potential as feedstock, using a gallosilicate catalyst<sup>1)</sup>. The catalytic process can be applied to the chemical recycling of chlorine free polyolefins. However, municipal waste plastics are mixtures of various types of polymers. Because of the difficulty of doing a complete separation of plastics by polymer type, a polyolefin fraction obtained from municipal waste plastics still contains small amounts of other polymers. Among them, PVC that generates HCl during its degradation process<sup>2), 3)</sup> may lower the activity of catalyst. Then, the catalytic degradation of polyolefins becomes a less effective recycling process. Hence, it is very crucial to develop a catalyst for the degradation of LDPE in the presence of PVC that combines chlorine tolerance with high activity.

In this study, commercially available LDPE (915 kg m<sup>-3</sup>, Ube Industries, Ltd.) and PVC (Showa Chemical Co., Ltd.) were used without further treatment. Polymers mixtures were prepared at concentrations of 0–1.0 wt% PVC. The degradation of the blends was carried out by the use of a batch reactor system consisting of two independent reaction zones. A 0.5 g sample was loaded in the first reactor and decomposed thermally at 455°C. The vapors of the thermal degradation products flowed

into the second reactor loaded with 0.1 g catalyst and catalytic cracking of the vapors was carried out at 525°C. The gaseous and liquid degradation products were analyzed by gas chromatography. A grease-like product was defined as wax and measured gravimetrically. The amount of coke deposited on the catalyst surface was determined by thermogravimetry. The catalysts used in the present study were H-gallosilicate (GaMFI, Si/Ga = 22.5) and H-galloaluminosilicate (GaAlMFI, Si/Ga = 28 and Si/Al = 51) supplied by Nippon Chemical Industrial Co., Ltd., and H-ZSM-5 (Si/Al = 15) supplied by N.E. CHEMCAT. Al<sub>2</sub>O<sub>3</sub>(1%)/GaMFI was prepared by impregnating GaMFI into an aluminum nitrate solution. The acidity of catalysts was evaluated by comparing their catalytic activity in the dealkylation of cumene at 250°C using a pulse reactor<sup>4)</sup> and NH<sub>3</sub>-TPD.

Figure 1 shows the yield of aromatics obtained from the degradation of PVC/LDPE mixtures using various catalysts. GaMFI catalyst exhibited a high activity for the degradation of LDPE into aromatic hydrocarbons, which were produced in minimal amounts in the thermal degradation. BTX accounted for most of the aromatics



**Fig. 1** Effect of Concentration of PVC on the Yield of Aromatics Produced from Degradation of PVC/LDPE

“ポリエチレンのケミカルリサイクルのための耐塩素性分解触媒の開発”

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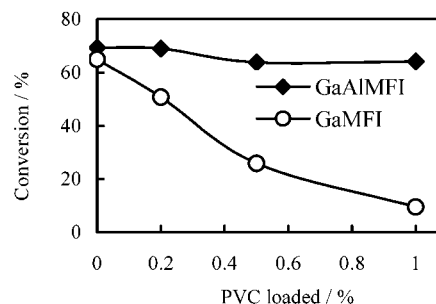
produced. However, the catalytic activity of GaMFI for the production of aromatics decreased with an increase in the concentration of PVC in the plastic mixture, suggesting that HCl produced from the decomposition of PVC caused catalyst deactivation. In contrast, H-ZSM-5 catalyst was less active than GaMFI for the degradation of LDPE into aromatics, but showed no significant loss of catalytic activity in the presence of PVC. From these results, we propose that Ga is the preferred element for attaining high aromatization activity and Al is the choice for achieving chlorine tolerance. To test the possible additive effects, GaAlMFI and  $\text{Al}_2\text{O}_3/\text{GaMFI}$  were prepared and employed as catalysts. The GaAlMFI synthesized hydrothermally was more active than GaMFI for converting LDPE into aromatics and showed a good tolerance to PVC. In the case of the  $\text{Al}_2\text{O}_3/\text{GaMFI}$  catalyst, where  $\text{Al}_2\text{O}_3$  is supported on the base catalyst, no improvement of the catalytic performance was observed. These results indicate that incorporation of Al into the silicate framework is of primarily importance for development of chlorine tolerance.

The product compositions produced by use of GaMFI and GaAlMFI were further compared (Table 1). More gas and less liquid and hydrogen were produced in the degradation of PVC/LDPE than LDPE over both catalysts. However, the change in the product composition for GaAlMFI was much less than that for GaMFI. The yield of aromatics in the degradation of PVC(1)/LDPE was 57.0% on GaAlMFI, compared to 61.6% in the degradation of LDPE.

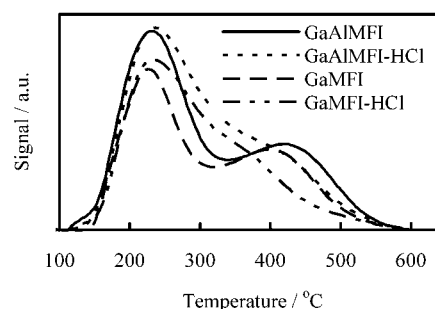
**Table 1** Composition of the Products in Catalytic Degradation of LDPE and PVC/LDPE

Catalyst PVC [wt%]	GaMFI		GaAlMFI	
	0	1.0	0	1.0
Yield [wt% feed]				
H <sub>2</sub>	3.3	2.5	3.4	3.0
Gas (C <sub>1</sub> -C <sub>4</sub> )	30.3	38.6	29.6	32.1
Liquid	63.0	51.2	63.6	59.2
Aromatics	58.5	41.9	61.6	57.0
Wax	3.0	5.6	3.0	3.7
Coke	0.4	0.6	0.5	0.5

To elucidate the influence of PVC on catalytic activity, the gallium catalysts were treated at 525°C with HCl, which was generated by decomposition of PVC alone at 300°C. The amount of PVC loaded, which corresponded to the PVC concentration in the plastic mixture, controlled the extent of the HCl treatment. Figure 2 shows the activity of the catalysts thus treated for dealkylation of cumene that is known to proceed on Brønsted acid sites. GaAlMFI exhibited a high activity even after the HCl treatment, while a large activity loss of GaMFI by HCl was observed. This suggests that HCl reduced the number of Brønsted acid sites originating from Ga atoms, but the acid sites originating from Al atoms were not greatly influenced by HCl, since Al



**Fig. 2** Dealkylation of Cumene on Ga Catalysts Treated with HCl Evolved from PVC



**Fig. 3** NH<sub>3</sub>-TPD Profiles of Ga Catalysts before and after HCl Treatment with PVC (1%)

oxide has a weaker affinity for HCl than does Ga oxide. Figure 3 shows NH<sub>3</sub>-TPD profiles of the catalysts before and after the treatment with HCl evolved from PVC. The amount of NH<sub>3</sub> desorbed in the high temperature region was decreased by HCl treatment, and was accompanied by an increase in the desorbed amount of NH<sub>3</sub> in low temperature region. The acidity of gallium catalysts was thus reduced by HCl, but GaAlMFI treated with HCl was still more acidic than GaMFI without HCl treatment. This may be a primary cause of the high activity of GaAlMFI in the presence of PVC.

In conclusion, GaAlMFI is a chlorine tolerant catalyst that shows good performance for the degradation of LDPE into aromatic hydrocarbons in the presence of PVC. The catalyst has a high potential for use in chemical recycling of waste plastics.

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