

# ゼオライト欠陥サイトへの $\text{Cr}^{6+}$ 導入によるコーキング抑制： 低密度ポリエチレン接触分解反応における再生処理削減

High coke deposition resistance by  $\text{Cr}^{6+}$  loading on zeolite defects:  
reduced regeneration in low-density polyethylene cracking

M23海自15

派遣先 第9回欧州ゼオライト学会（スロベニア・ポルトロシュ）

期 間 2023年7月1日～2023年7月7日（7日間）

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## 海外における研究活動状況

### 研究目的

廃プラスチックを化学的に分解し、原料化するケミカルリサイクル（CR）が注目されており、プラスチック資源の循環を実現する方法として期待されている。

ゼオライトは、固体酸性や規則的な細孔構造といった優れた性質を持つことから、CRへの応用に向け盛んに研究が行われている。しかし、ゼオライトの酸性質を利用した反応ではコークが析出し、触媒が劣化する。これまでにコーク析出抑制に向け様々な策が講じられてきたが、プラスチック分解に応用可能な手法は未だ開発されていない。そのため、プラスチック分解活性を維持したままコーク析出を抑制する新たな手法が必要である。

申請者は、ゼオライト中に $\text{Cr}$ 導入することで、プラスチック分解反応において、分解活性を維持したままコーク析出を大幅に抑制することに成功した。また、開発した触媒は、焼成による再生処理を実用とせず、繰り返し使用しても活性が低下しないことを確認した。

### 海外における研究活動報告

The increase in plastic waste has induced critical environmental problems, thereby plastic waste should be managed better than ever. Chemical recycling (CR) has recently been considered as an attractive candidate to solve this problem<sup>1</sup>. In CR, plastic wastes can be converted into valuable products (e.g., monomers or petrochemical feedstocks). Recently, there has been much research on the catalytic cracking of polymers using zeolites. However, the deactivation of zeolites due to coke deposition is a serious problem. Although significant efforts have been devoted toward coking inhibition, the previous methods are not suitable for polymer cracking. Therefore, new approaches are needed to inhibit coke deposition without degrading catalytic performance.

Recently, it has been reported that  $\text{Cr}^{6+}$  connected to silanol groups in zeolites is stable and promotes the dehydrogenation of light alkanes<sup>2</sup>. Since many alkanes are produced in the catalytic cracking of polyolefins, these alkanes are considered dehydrogenated during the reaction. Moreover, aromatics, which are coke precursors,

are decomposed via hydrogenation on acid sites of the zeolite. Therefore, hydrogen is generated from the alkanes in the product at the  $\text{Cr}^{6+}$  sites, and the hydrogenation and decomposition of the coke precursor at the zeolite acid sites are thought to have inhibited coke deposition. In this study, Beta zeolite was doped with  $\text{Cr}^{6+}$ , and the effect of the synthesized catalysts on coke inhibition was examined by the catalytic cracking of low-density polyethylene (LDPE).

We prepared Cr/Beta( $x$ ) samples at a mass ratio of  $\text{Cr}/\text{Beta} = x/100$  ( $x = 0.1, 0.5, 1, 5$ , and  $10$ ) by the impregnation method.

UV-Vis spectroscopy was conducted to investigate the valency of Cr species in zeolites. The absorption band derived from  $\text{Cr}^{3+}$  was only detected for Cr/Beta(5) and Cr/Beta(10), indicating the presence of  $\text{Cr}_2\text{O}_3$ . Moreover, the peaks derived from  $\text{Cr}^{6+}$  were detected for all Cr-loaded samples. We conducted FT-IR spectroscopy to investigate the detailed chemical states of the  $\text{Cr}^{6+}$  species. The Cr/Beta samples showed peaks attributed to the Si-O- $\text{Cr}^{6+}$  vibration. Moreover, the weak band assigned to the Cr-O or Cr=O vibration in the  $\text{Cr}^{6+}$  species was observed. Thermogravimetric (TG) curves for the catalytic cracking of LDPE under  $\text{N}_2$  flow at a heating rate of  $5 \text{ K min}^{-1}$  were measured to investigate the catalytic performance of Cr/Beta.

The decomposition temperature increased slightly when the Cr loading was higher than 5 wt.%, but the Cr loading did not significantly decrease the catalytic activity of Beta zeolite.

In the reaction,  $\text{Cr}^{6+}$  species connected to silanol groups performed as a catalyst for the dehydrogenation of light alkanes in the products, and aromatics were decomposed via hydrogenation at the zeolite acid sites. In the ethane dehydrogenation reaction, Cr/Beta generated  $\text{H}_2$  at a lower temperature than pristine Beta. And it was confirmed that coke precursor was decomposed at zeolite acid sites by using toluene and cyclohexane. Therefore, the synergetic effect of the  $\text{H}_2$  generation by  $\text{Cr}^{6+}$  and the decomposition of coke precursor by zeolite acid sites led to coking inhibition. As a result, it was possible to recycle the obtained catalysts several times without regeneration during the catalytic cracking of LDPE.

この派遣の研究成果等を発表した  
著書、論文、報告書の書名・講演題目

S. Kokuryo, K. Tamura, K. Miyake, Y. Uchida, M. Miyamoto, Y. Oumi, A. Mizusawa, T. Kubo, "High coke deposition resistance by Cr loading on zeolite defects: reduced regeneration in cracking reactions," Catal. Sci. Technol., 2022, 12, 7270-7274.