Investigation of deactivation factor of $CuCl_2$-KCl/Al_2O_3 catalyst for ethylene–oxychlorination in commercial scale plant

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Abstract: Two years consecutive examination of the ethylene oxychlorination over a $CuCl_2$-KCl/Al_2O_3 catalyst was operated in the scale of commercial plant. The oxychlorination performance of the catalyst was gradually deactivated. In order to clarify such deactivation factors of the catalyst, the relationship between the catalyst performance and the physicochemical property change of the catalyst was investigated. A sublimation of CuCl component and a subsequent increment of the ratio of K to Cu components were clearly observed at the inlet of the catalyst bed. Such sublimation and component change would be one of the factors of deactivation of the $CuCl_2$-KCl/Al_2O_3 catalyst.

Keywords: Oxychlorination, deactivation, activation energy.

1. Introduction

A balanced oxychlorination process is mainly used as the vinyl chloride monomer (VCM) manufacturing. In this process, the main reaction is consisted by three reactions as shown in Scheme1. The point of oxychlorination is recycling hydrogen chloride as various reaction by-products.

Figure 1. Vinyl chloride monomer plant.

Scheme 1

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 \quad (1)$$

$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl \quad (2)$$

$$C_2H_4 + 2HCl + 1/2O_2 \rightarrow C_2H_4Cl_2 + H_2O \quad (3)$$

In the industrial oxychlorination process, copper-based chloride catalyst have traditionally been used due to its high activity and high selectivity of ethylenedichloride (EDC), comparing with another transition metal [1]. However, because the oxychlorination of ethylene is a large exothermic reaction, the generated heat damage accelerated the deactivation of the copper-based chloride catalyst. Therefore, the addition technique of alkali metal chloride and/or alkaline earth metal chloride was usually adopted so as to improve the durability performance [2]. Our company has succeeded in operated a long-term plant manufacturing using this catalyst.

In this study, using the $CuCl_2$-KCl/Al_2O_3 catalyst sampled from the actual plant equipment, deterioration factors were estimated from the correlation between the physicochemical analysis (component, surface area, element distribution et al.) and the activity in the long term operation. In addition, we also focused on the relationship between the increase in activation energy and catalyst deterioration, and investigated to lead to the prediction of plant life from the changing behavior of activation energy.

2. Experimental

The $CuCl_2$-KCl/Al_2O_3 catalyst was prepared by impregnation of a γ-alumina（extruded to cylinder-shape, surface area $184 m^2g^{-1}$, pore volume $0.62 mlg^{-1}$）into aqueous solutions of copper chloride and potassium chloride. After impregnation, the catalyst was dried at 423K for 2h, followed calcination at 523K for 5h. The resultant catalyst was 13.1wt%$CuCl_2$-4.9wt%KCl/Al_2O_3, surface area $112 m^2g^{-1}$, pore volume $0.30 mlg^{-1}$.This fresh catalyst was subjected to an endurance test in a commercial plant. After two years operation, the catalyst layer was divided into five positions from the inlet and labeled as 1st (inlet), 2nd, 3rd, 4th, 5th (outlet), respectively. The chemical properties of fresh and used catalysts were evaluated using a fixed-bed reactor and some instruments.

3. Results and discussion

Fig.2 shows the oxychlorination activity and physical properties (BET, copper content) of the catalyst sampled from each position of the reactor. The activity shown in here is the relative activity basing on the initial catalyst performance as 100%. The catalyst sampled from the inlet side (1st, 2nd) was clearly deactivated, but that from the middle (3rd, 4th) and the outlet (5th) were not so declined. The tendency of activity is almost corresponded as the order of copper content, although the BET specific surface was not coincided. It was suggested that the sublimation of copper component, caused by high exothermic energy profile at the inlet side, was one of the factors of deactivation of the $CuCl_2$-KCl/Al_2O_3 catalyst [3, 4]. The obtained data provides some valuable information indicating the catalytic behavior in a commercial plant.

Fig.3 shows the relationship between the ratio of potassium and copper elements (K/Cu) and the activation energy of the fresh and used catalysts, which was estimated by a kinetic study. The activation energy of the fresh catalyst was about 56 kJ/mol closed to the reported value (63 kJ/mol, Fujimoto et al. [5]). For all sampled catalyst, it was clearly found that the increment of the K/Cu ratio correlated to the increment of activation energy, suggesting the deactivation of the oxychlorination catalyst. Furthermore, this increment trend of activation energy has been able to be utilized for prediction of the catalyst life in the plant. Such lifetime prediction has been greatly contributed to stable operation and production management of the oxychlorination plants.

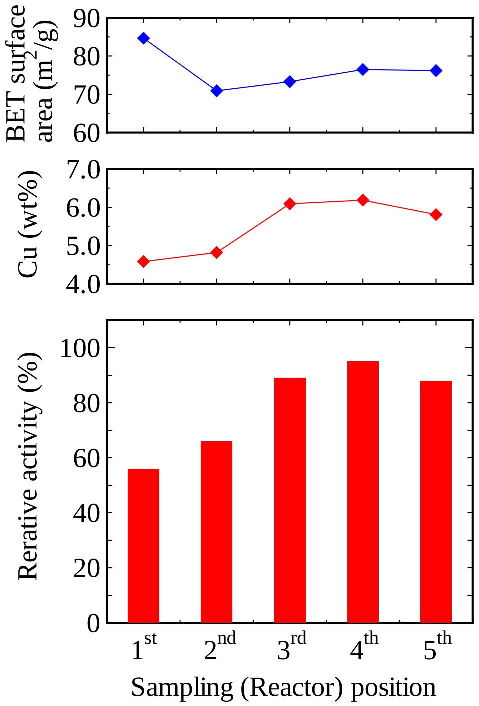

Figure 2. Oxychlorination performance change of the catalysts sampled from various reactor position.

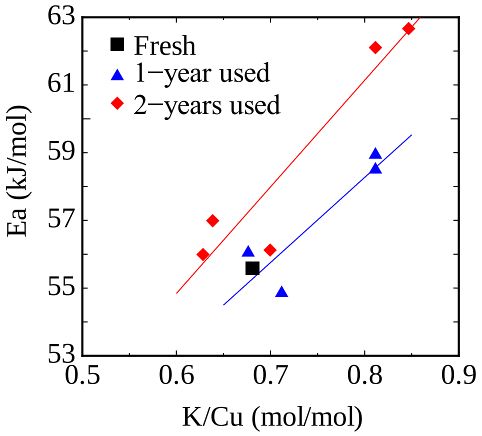

Figure 3. Relationship between activation energy and ratio of K/Cu component.

4. Conclusions

Using the oxychlorination catalyst operated during two years in the commercial plant, the relationship between deactivation and physical property change of the catalyst was investigated. The increment of K/Cu ratio caused by sublimation of copper brought about the catalyst deactivation with an increase in activation energy. This increment trend of activation energy has been able to utilize for prediction technology of the plant operation.

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