XANES analysis of $CuCl_2$-KCl/Al_2O_3 catalyst operated in commercial ethylene-oxychlorination process

Sae Someya[a]*, Tomokazu Ohashi,[a] Yoshihiko Mori[a], Tetsuo Asakawa[a], Makoto Hanaya[a], Motohiro Oguri[a], Ryo Watanabe[b], Choji Fukuhara[b].

[a] *Functional polymers research laboratory, Tosoh Corporation,1-8 Kasumi, Yokkaichi, Mie 510-8540, Japan*

[b] *Graduate school of Applied Chemistry and Biochemical Engineering, Shizuoka University, Shizuoka, 432-8561, Japan*

**Corresponding author: Fax number: +81-59-364-5546, E-mail address: sae-someya-jw@tosoh.co.jp*

Abstract: The $CuCl_2$-KCl/γ-Al_2O_3 catalyst is utilized in the industrial oxychlorination plant owned by Tosoh Corporation. Over the two-year operation, the $CuCl_2$-KCl/γ-Al_2O_3 catalyst indicated a deactivation from about 60 % (inlet part) to about 90 % (outlet part) compared with the initial activity. In order to investigate the deactivation factors, the Cu composition in the used catalyst was analyzed by XANES. Linear-combination fitting of XANES spectra showed that the amount of $CuCl_2$ was decreased and that of $KCuCl_3$ was increased. The formation of $KCuCl_3$ from $CuCl_2$ compound is considered to be a deactivation factor in the long-term operation of the oxychlorination plant.

Keywords: Oxychlorination, Deactivation, XANES.

1. Introduction

Ethylene-oxychlorination is an important reaction for synthesizing 1,2-dichloroethane (EDC) utilized for an intermediate material of vinyl chloride monomer (VCM). The EDC is annually produced by 20 million tons via oxychlorination of ethylene. In this reaction, the $CuCl_2$/γ-Al_2O_3 catalyst is industrially utilized for several decades.[1] The proposed catalyst cycle is expressed by the following equations.

$$2\ CuCl_2 + C_2H_4 \rightarrow C_2H_2Cl_2\ (EDC) + 2CuCl \quad (1)$$

$$2CuCl + 1/2\ O_2 \rightarrow Cu_2OCl_2 \quad (2)$$

$$Cu_2OCl_2 + 2HCl \rightarrow 2\ CuCl_2 + H_2O \quad (3)$$

The active phase of $CuCl_2$ reacted with C_2H_4 to produce EDC and a reduced phase of CuCl. The CuCl component was oxidized to produce Cu_2OCl_2, and followed by the chlorination of Cu_2OCl_2 to $CuCl_2$. The $CuCl_2$/γ-Al_2O_3 catalyst shows a high performance due to a smooth redox cycle, however this catalyst was thermally unstable in the reaction atmosphere. Therefore, the KCl was added to improve a thermal stability of the $CuCl_2$/γ-Al_2O_3 (abbreviated as $CuCl_2$-KCl/γ-Al_2O_3) catalyst, which was utilized in the industrial oxychlorination plant owned by Tosoh Corporation. The $CuCl_2$-KCl/γ-Al_2O_3 catalyst is highly-active and selective to produce EDC. However, over the two-year operation, its performance declined from about 60 % (inlet part) to about 90 % (outlet) compared with the initial activity.

In this study, the condition of Cu component in the operated $CuCl_2$-KCl/γ-Al_2O_3 catalyst was analyzed using XANES analysis. The obtained spectra were deconvoluted in detail by a linear-combination fitting method to detect the deactivated phase on the catalyst.

2. Experimental

The $CuCl_2$-KCl/γ-Al_2O_3 catalyst was prepared by a conventional impregnation method. The loading amounts of $CuCl_2$ and KCl were respectively 13.1 wt% and 4.9 wt%. The elemental analysis of the two-year operated catalyst was performed using XRF (Rigaku ZSX PrimusII). The Cu *K*-edge XANES analysis was carried out using BL5S1 at the Aichi Synchrotron Radiation Center (Aichi, Japan). The sample was prepared as follows: the used catalyst was extracted from the industrial plant, and followed by the oxychlorination atmosphere for 8 h in the fixed-bed reactor, where we checked the catalyst performance under the gas volume ratio of $HCl:C_2H_4:O_2:N_2$=2.0:1.0:0.4:2.8 and GHSV of 400 h^{-1}. Subsequently, the prepared sample was sealed under the vacuum condition without any exposure to air. The ring energy was 1.2 GeV and the current value

was 300 mA. The spectrum was obtained using the transmission mode at room temperature. In order to deconvolute the XANES spectra, REX-2000 (Rigaku) software was used.

3. Results and discussion

In order to clarify the deactivation process of the $CuCl_2$-KCl/γ-Al_2O_3 catalyst, two-type catalysts were prepared. One is the catalyst extracted from the inlet part of the plant, of which activity was about 60-80 % based on the fresh catalyst, and another is that from the outlet part, of which activity was about 90-100 %. It is noted that there is a large difference in the amount of copper component on the two catalysts due to volatilization of Cu component. Fig. 1(a) shows XANES spectra for these two samples, which were respectively abbreviated as catalyst (inlet) and catalyst (outlet). As a result, XANES spectra were almost identical for these two catalysts. The shapes of XANES spectra for the both catalysts were similar to that of $CuCl_2$ and $KCuCl_3$ species. Such result indicated that the main component of the catalyst was $CuCl_2$ and/or $KCuCl_3$ species. These spectra were deconvoluted in detail by a linear-combination fitting method to detect the deactivated phase on the catalyst. Four compounds such as $CuCl_2$, CuCl, $KCuCl_3$ and $CuAl_2O_4$ were considered as the component in the $CuCl_2$-KCl/γ-Al_2O_3.

Fig. 1(b) describes the fraction of the Cu compounds in the catalyst as a function of the catalytic activity. The fraction of $CuCl_2$ was clearly increased as the deactivation was suppressed. The components of $KCuCl_3$ and $CuAl_2O_4$ were increased in the deactivated catalysts. Since $CuAl_2O_4$ was inert species for oxychlorination, $CuCl_2$ and $KCuCl_3$ were considered as the major species for affecting on the catalytic activity. The $CuCl_2$ was known to be the active phase on chlorination of ethylene because of the high redox property.[3] The formation $KCuCl_3$ from $CuCl_2$ was considered as one of main factors in the deactivation for ethylene-oxychlorination.

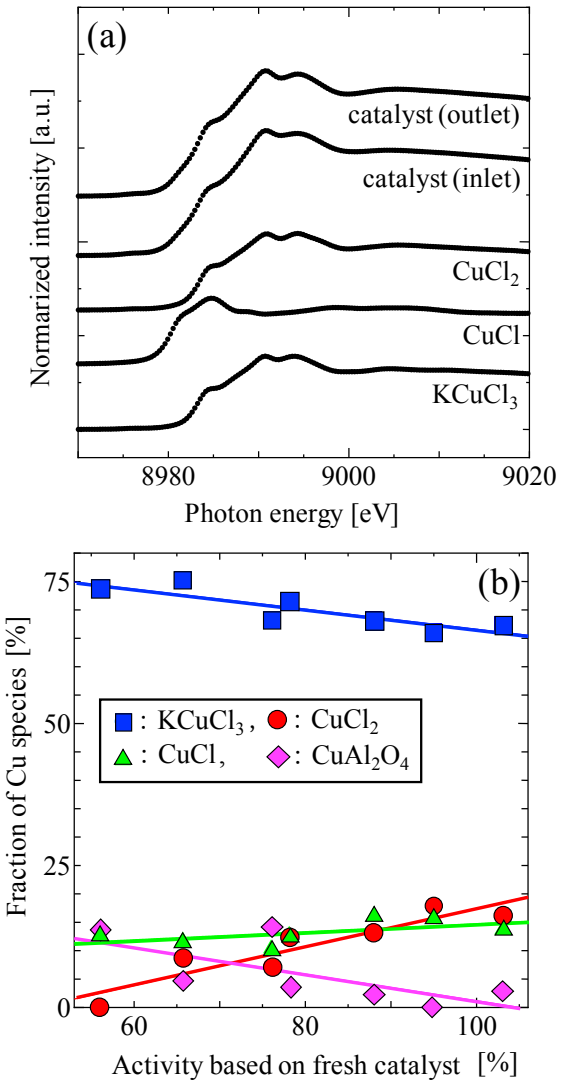

Figure 1. (a) XANES spectra of Cu *K*-edge, (b) fraction of copper species of activated and deactivated catalyst evaluated from XANES linear-combination fitting on activity based on fresh catalyst.

4. Conclusions

The Cu *K*-edge XANES analysis was carried out over the two-year operated $CuCl_2$-KCl/Al_2O_3 catalyst in the commercial plant as to investigate deactivation process. Linear-combination fitting clearly showed that $CuCl_2$ was decreased and $KCuCl_3$ was increased with deactivation. $CuCl_2$ was known as more active phase on ethylene-chlorination than $KCuCl_3$. Therefore, the decrease of $CuCl_2$ was considered as long-term deactivation factor on oxychlorination.

1. P. G. Hall, M. Parsley, D. R. Rosseinsly, R. A. Hann, K. C. Waugh, J. Chem. Soc. Faraday Trans. 1 79 (1983) 343.
2. N. B. Muddada, U. Olsbye, *et al*, Lamberti, Dalton Trans. 39 (2010) 8437.
3. N. B. Muddada, U. Olsbye, *et al*, Phys. Chem. Chem. Phys. 12 (2010) 5605.