Characterization of fluorinated alumina based on acid properties and structures

Taku Yamada,[a]* **Tatsuya Miyajima**[b]
[a] *New Product R&D Center, Asahi Glass Co., Ltd., Yokohama, Japan*
[b] *Innovative Technology Research Center, Asahi Glass Co., Ltd., Yokohama, Japan*
** Corresponding author: Fax: +81-45-374-8805, E-mail: taku-yamada@agc.com*

Abstract: The systematic study for the acid properties and crystal structures of partially fluorinated alumina (aluminum oxide) catalysts being different in content of fluorine. The partially fluorinated alumina catalysts which have almost the same amount and strength of Lewis acidity were independent of the fluorine contents. These catalysts in the same structure as aluminum fluoride hydroxides changed from AlF_3O_3 to AlF_5O via AlF_4O_2 in composition with the increase of fluorine contents.

Keywords: Lewis acid catalyst, Fluorinated, Fluorinated alumina.

1. Introduction

Metal fluorides such as aluminum fluoride (AlF3), chromium fluoride (CrF3) and so on have been established as the important fluorinated catalysts in the industrial processes for the production of such fluorocarbon materials as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). Dehydrohalogenation (dehydrochlorination and dehydrofluorination), isomerization between chlorine and fluorine [1] and Friedel-Crafts-type alkylation [2] have been accomplished using many kinds of metal fluorides. Among the world-wide efforts to prevent global warming and ozone layer depletion in recent years, hydrofluoroolefins (HFOs) and hydrochlorofluoroolefins (HCFOs) have been produced as the next generation alternatives. The *E-Z* isomerization reactions through the metal fluorides have been also reported for the production of HFO-1234ze [3] and HCFO-1233zd [4]. These metal fluorides catalysts have been prepared under the fluorination of the corresponding metal oxides passing fluorinated materials such as hydrogen fluoride (HF), fluorine (F2), ammonium fluoride (NH_4F), CFCs, HCFCs, and so on[5]. The evaluation of the difference between the catalyst states based on the analytical techniques should be essential toward the investigation of catalytic activity and mechanism for the target reactions. Here, the systematic investigation for the fluorinated alumina catalysts would be discussed in the basis of their acid properties and crystal structures.

2. Experimental

Partially fluorinated alumina catalysts were prepared by contacting alumina with fluorine-containing compounds (e.g. fluorocarbons) at high temperature. These catalysts were characterized by pyridine adsorption IR (infrared) analysis, ammonia-TPD (temperature-programmed desorption) analysis, XRF (X-ray fluorescence), XRD (X-ray diffraction), and ^{27}Al- and ^{19}F-MAS NMR (magic angle spinning nuclear magnetic resonance). The evaluation of hydroxyl (OH) group and the type of acid sites on the catalysts were carried out by means of transmission type infrared spectrometer Nicolet-380 (Thermofisher). The amount and strength of Lewis acidity for the catalysts were determined by ammonia (NH_3)-TPD analysis using BELCATII (Microtrac-Bel), BELMass (Microtrac-Bel), detecting ammonia at m/z=16. The catalyst composition was determined by XRF using ZSX 100e (Rigaku). The XRD measurements were carried out using SmartLab (Rigaku). ^{27}Al MAS NMR was measured using ECA 600 (JEOL) and ^{19} F MAS NMR was measured using AVANCE-III (Bruker Bio Spin) to obtain the structural information for their catalysts.

3. Results and discussion

All of the prepared fluorinated alumina catalysts were identified as the crystal structure in aluminum fluoride hydroxide $AlF_x(OH)_{6-x}$ by XRD analysis. From the results of XRF analysis, it was confirmed that their catalysts had differences in the contents of fluorine. In the evaluation for acid properties, the NH3-TPD analysis indicated only a very slight difference in both amount and strength of acidity. On the other hand, it was indicated that the interaction between pyridine and the fluorinated alumina catalysts was decreased with the increase of fluorine contents from the results of the pyridine absorption IR analysis. Their results was also indicated that all of the catalysts had only the Lewis acidity without Brønsted acidity. Catalysts with lower content of fluorine were clearly found to have the IR absorption for hydroxyl (OH) group, although highly fluorinated alumina catalysts exhibited no absorption in the wavelength for OH group. ^{27}Al- and ^{19}F-MAS NMR in the solid state was performed to determine the coordination number of fluorine atoms coordinated on aluminum atom. It was found that all of their catalysts consisted of aluminum fluoride hydroxides such as AlF_3O_3, AlF_4O_2 and AlF_5O at the different composition ratios.

4. Conclusions

We systematically investigated about the variation for the acid properties and crystal structures of partially fluorinated alumina catalysts with different fluorine contents by use of various kinds of analysis methods. Although there was only a very slight difference in the acid properties of the catalysts, alumina was changed to the aluminum oxide fluoride structures by replacing by fluorine atoms. Depending on the fluorine contents, the significant changes in the type of ligands bonded to aluminum metal center and the amounts of hydroxyl groups were observed. It was suggested that the fluorine replacement for the ligands bonded to Al center proceeded easier for OH group than oxygen in the crystal lattice. Based on these results, the suitable control of the fluorine content into aluminum fluoride hydroxides would enable to control the activity and selectivity for the fluorination reaction via the fluorinated metal oxides.

References

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