Investigation of the catalytic activity for acid reactions over high-dimensional Nb oxide containing fluoride

Satoshi Ishikawa, [a] **Mai Shinoda,**[a] **Norihito Hiyoshi,**[b] **Wataru Ueda**[a]*

[a]*Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama, 221-8686, Japan*

[b]*National Institute of Advanced Industrial Science and Technology (AIST), 4-2-1 Nigatake, Miyagino, Sendai 983-8551, Japan*

**Corresponding author: 045-481-5661, uedaw@kanagawa-u.ac.jp*

Abstract: Effects of fluoride ion (F^-) on the formation of high-dimensional Nb oxide (HDS-NbO_x) were investigated. The addition of F^- up to $F^-/Nb \leq 0.5$ mol% promoted the crystal formation of HDS-NbO_x, while further F^- addition caused the formation of hexagonal Nb oxide (He-NbO_x). Catalytic activity over F^- containing HDS-NbO_x for various Brønsted acid reactions increased with the F^- amount, but the activity suddenly dropped when He-NbO_x started to form. Based on the observed dependency between the crystal structure and the catalytic activity, catalysis field over HDS-NbO_x could be proposed.

Keywords: Hydrothermal synthesis, Nb oxide, Acid reaction.

1. Introduction

Niobium oxide (NbO_x) has been attracting much attention as an effective heterogeneous catalyst for various acid reactions, including alkylation, isomerization, esterification, hydrolysis and dehydration[1-2]. Much effort has been devoted to understand the attractive acid property over NbO_x for a long time. However, in spite of the tremendous efforts, clear conclusion about the origin of the acid catalytic activity has not been achieved up to the date. This situation is largely derived from the amorphous nature of NbO_x which makes the investigation of active site difficult. Recently, we reported that high-dimensional NbO_x (HDS-NbO_x) formed under hydrothermal condition showed far better catalytic activity for Friedel-Crafts alkylation (Brønsted acid reaction) than those of other NbO_x catalysts with different crystal phase. This observed structure-activity relationship implied that the catalytic activity over HDS-NbO_x is derived from the nano-scale local catalyst structure. Here, we report that the addition of fluoride ion (F^-) promoted the crystal formation of HDS-NbO_x, which enhanced the catalytic activity for various Brønsted acid reactions. Based on the characterization results and the catalytic activity trend, the catalytically active site over HDS-NbO_x for Brønsted acid reactions could be proposed.

2. Experimental

The precursor solution prepared by dissolving ammonium niobium oxalate ($NH_4[NbO(C_2O_4)_2(H_2O)]\cdot nH_2O$ (CBMM), Nb: 6.0 mmol) and NH_4F (0, 0.6, 1.2, 1.8, 2.4, 3.0, 4.2 and 6.0 mmol) in 40 mL of deionized water was subjected to the hydrothermal synthesis at 175 °C for 72 h. Obtained materials were abbreviated as HDS-NbO_x-*a*F, where *a* indicates the molar ratio of F^-/Nb (*a* = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7 and 1.0). Friedel-Crafts alkylation was carried out as a model acid reaction. Reaction condition: catalyst amount, 10 ~ 30 mg; reaction temperature, 100 °C; anisole/benzyl alcohol/decane (internal standard) = 44.6/1.0/0.5 mmol.

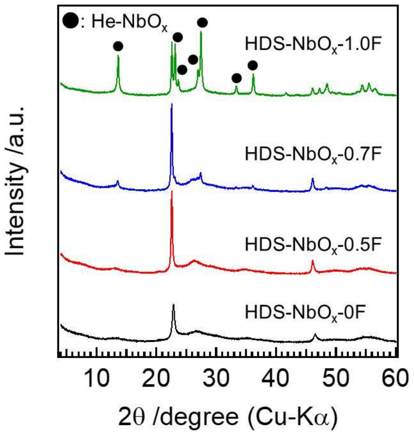

Figure 1. XRD patterns of HDS-NbO_x-*a*F.

3. Results and discussion

XRD patterns of HDS-NbO_x-aF (a = 0, 0.5, 0.7 and 1.0) are shown in Figure 1. HDS-NbO_x-0F showed two main XRD peaks at 2θ = 22.7° and 46.2° attributable to (001) and (002) planes, respectively, indicating the formation of HDS-NbO_x[1]. The intensity of these peaks were considerably increased by the addition of F^-. However, the addition of F^- up to a = 0.7 caused the formation of the hexagonal Nb_2O_5 (He-NbO_x) and the peak intensity of He-NbO_x increased by the further F^- addition. Then, TEM and HAADF-STEM analyses were carried out and the obtained results are shown in Figure 2. TEM images of HDS-NbO_x-0F and HDS-NbO_x-0.5F showed that both the materials were rod-shaped materials. However, the size of the rod-shaped materials was much different and the average diameter of the rod was 5.7 nm in HDS-NbO_x-0F and 14.0 nm in HDS-NbO_x-0.5F, respectively. The increased crystal size could be also confirmed by the decrease of BET surface area (HDS-NbO_x-0F, 222 m^2 g^{-1}; and HDS-NbO_x-0.5F, 163 m^2 g^{-1}). HAADF-STEM image of HDS-NbO_x-0F in the [001] projection showed the disordered arrangement of pentagonal $\{Nb_6O_{21}\}$ units which resulted in the formation of the heptagonal channel in the structure. The pentagonal $\{Nb_6O_{21}\}$ units in HDS-NbO_x-0.5F were well isolated for each other which increased the density of the heptagonal channel (The numbers of heptagonal channel per area: HDS-NbO_x-0F, 0.6 /nm^2; HDS-NbO_x-0.5F, 2.4 /nm^2). The above facts clearly indicate that the addition of F^- promoted the crystallization of HDS-NbO_x and increased the number of heptagonal channels in cross-section of the rod up to F^-/Nb $\leq$ 0.5 mol%. Figure 3 shows the relationship between preparative F/Nb ratio and the reaction rate per surface area for Friedel-Crafts alkylation over HDS-NbO_x-aF. The reaction rate was increased with increasing a in the range of $0 \leq a \leq 0.5$, but was decreased in $0.7 \leq a$. Almost the same trend could be observed in the different Brønsted acid reactions such as α-pinene isomerization and cyclization of citronellal. The observed trend implies that the heptagonal channel in the catalyst structure works as a catalytically active site for Brønsted acid reactions.

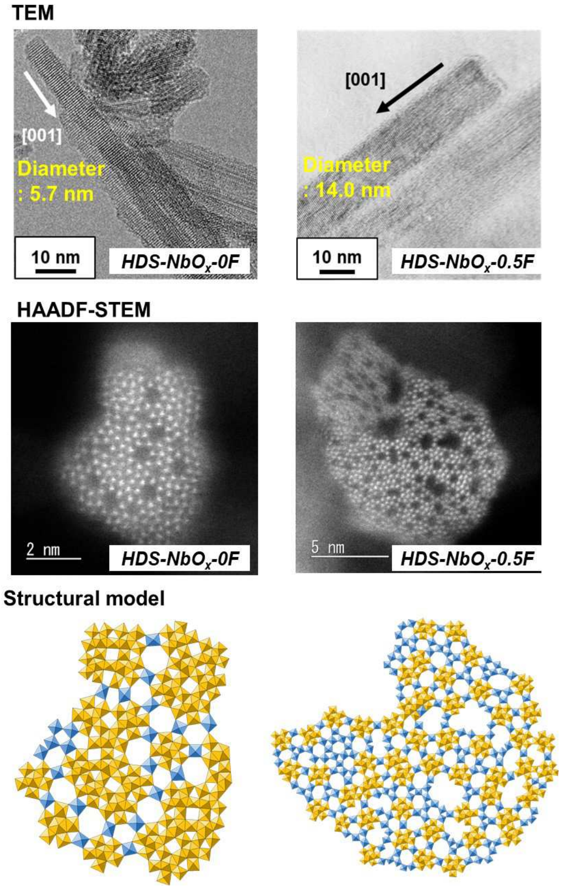

Figure 2. TEM images, HAADF-STEM images and structural model of HDS-NbO_x-0F and HDS-NbO_x-0.5F. Yellow units in the structural model are pentagonal $\{Nb_6O_{21}\}$ unit

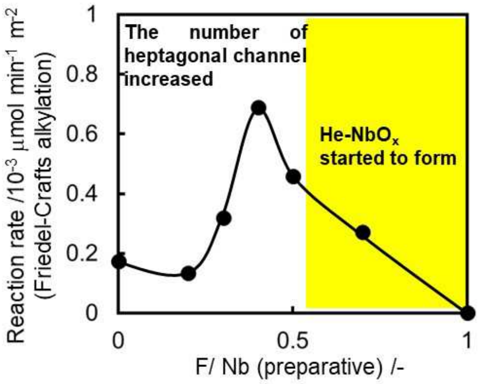

Figure 3. Relationship between preparative F/Nb ratio and reaction rate per surface area for Friedel Crafts alkylation.

4. Conclusions

Based on the above facts, we could propose that the heptagonal channel site over HDS-NbO_x is responsible for catalyzing Brønsted acid reactions.

References

1. T. Murayama, J. Chen, J. Hirata, K. Matsumoto, W. Ueda, Catal. Sci. Technol. 4 (2014) 4250.
2. T. Kitano, T. Shishido, K. Teramura, T. Tanaka, J. Phys. Chem. C 116 (2012) 11615.