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

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

Keywords: Hydrothermal synthesis, Nb oxide, Acid reaction.

1. Introduction

Niobium oxide (NbOₓ) has been attracting much attention as an effective heterogeneous catalyst for various acid reactions, including alkylation, isomerization, esterification, hydrolysis and dehydration. Much effort has been devoted to understand the attractive acid property over NbOₓ 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 NbOₓ which makes the investigation of active site difficult. Recently, we reported that high-dimensional NbOₓ (HDS-NbOₓ) formed under hydrothermal condition showed far better catalytic activity for Friedel-Crafts alkylation (Brønsted acid reaction) than those of other NbOₓ catalysts with different crystal phase. This observed structure-activity relationship implied that the catalytic activity over HDS-NbOₓ is derived from the nanoscale local catalyst structure. Here, we report that the addition of fluoride ion (F⁻) promoted the crystal formation of HDS-NbOₓ, 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-NbOₓ for Brønsted acid reactions could be proposed.

2. Experimental

The precursor solution prepared by dissolving ammonium niobium oxalate (NH₄[NbO(C₂O₄)₂(H₂O)]·nH₂O (CBMM), Nb: 6.0 mmol) and NH₄F (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-NbOₓ-aF, 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.

3. Results and discussion

Figure 1. XRD patterns of HDS-NbOₓ-aF.
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 2$\theta$ = 22.7° and 46.2° attributable to (001) and (002) planes, respectively, indicating the formation of HDS-NbO$_x$. 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$_2$O$_5$ (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$_6$O$_{21}$} units which resulted in the formation of the heptagonal channel in the structure. The pentagonal {Nb$_6$O$_{21}$} 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 $\alpha$-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.

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