HNb_3O_8 nanosheet derived from amorphous niobic acid: Effect of layer stacking on the catalytic activity

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Abstract: HNb_3O_8 nanosheet was prepared by using amorphous niobic acid (NBA), where the solid-state and liquid synthesis methods were employed. NBA-derived nanosheets were evaluated to be much stable in the dehydration reaction compared to the analogues prepared by crystalline Nb_2O_5. In order to understand this difference, the samples obtained in each preparation step such as the mixing of K and Nb sources, calcination, proton exchange, and exfoliation/aggregation were analyzed by XRD, SEM, TEM-EDS, pyridine-IR, TG-MS, etc. The characterization results revealed that NBA-derived HNb_3O_8 nanosheet consisted of more stacked layers due to the presence of K^+ ions remaining in the exfoliated sample.

Keywords: Amorphous niobic acid, Potassium ions, Nanosheet durability

1. Introduction

Among various transition metal oxide nanosheets, much attention has been paid to HNb_3O_8 nanosheet in order to understand unique acid properties of niobic acid.[1–2] However, the synthesis is a multistep process including solid-state mixing, thermal treatment, proton exchange and exfoliation/aggregation, which shows a low product yield. Thus, we developed a new "liquid synthesis" method involving the contact of crystalline Nb_2O_5 solid with aqueous K_2CO_3 solution.[3] This method resulted in the high exfoliation efficiency and product yield, originating from the formation of homogeneous K_2CO_3–Nb_2O_5 mixture with more infiltrated K^+ ions and, in turn, potassium niobate structure (KNb_3O_8) with more intercalated K^+ ions. On the basis of our previous observation, we started to work on the use of different niobium source, that is, amorphous niobic acid (NBA) in the preparation of HNb_3O_8 nanosheet because the infiltration of K^+ ions would be more favored in amorphous NBA structure compared to crystalline Nb_2O_5 structure. As far as we know, this strategy has been not reported in literature.

2. Experimental

For the conventional solid-state synthesis, K_2CO_3 was ground with Nb_2O_5 or niobic acid supplied by CBMM (HY-340) using a mortar and pestle (K:Nb molar ratio = 1/3), and then ball-milled for 3 days. The resulting mixture was subjected to calcination at 1373 K for 5 h, followed by ion exchange with HNO_3 solution for 72 h at room temperature. After through washing with distilled water, H^+-exchanged niobate was added to tetrabutylammonium hydroxide solution for exfoliation and stirred under ambient condition. To this suspension, an aqueous HNO_3 solution was added for the recovery of exfoliated HNb_3O_8 as aggregates. The resulting white sample was collected by vacuum filtration, washed with distilled water and finally dried. This dry sample is referred to as NS Nb_2O_5 (S) or NS NBA (S), where (S) represents the solid-state synthesis. For the liquid synthesis, each niobium source was added into an aqueous K_2CO_3 solution, followed by vigorous stirring and drying at 373 K overnight. The subsequent steps were conducted identically as mentioned above, yielding NS Nb_2O_5 (L) and NS NBA (L) in which (L) represents the liquid synthesis.

The activities of the prepared samples were tested in the 2-heptanol dehydration using a high pressure batch reactor. Prior to the activity test, the sample was thermally treated at 723 K in N_2 atmosphere. After the reaction at 513 K for 6 h under N_2, the reaction mixture was taken out, filtered through a syringe filter and mixed with a GC standard of acetone. An aliquot of this solution was analyzed in a gas chromatograph.[3]

3. Results and discussion

In three consecutive runs for the dehydration of 2-heptanol (Fig. 1a), NS NBA (S) held the conversion of ca. 7.8% and NS NBA (L) showed a slight decrease in the conversion from 24.7% to 22.6%, which is different from parent NBA. However, a large activity decline was observed in both NS Nb_2O_5 (S) and (L). These results indicate that the durability of HNb_3O_8 nanosheet is influenced by the niobium source employed.

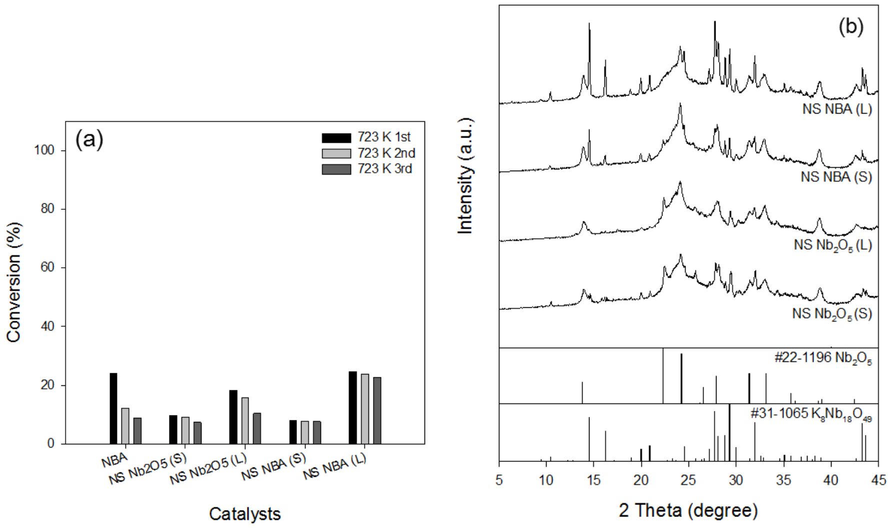

Figure 1. (a) Durability test in the dehydration of 2-heptanol and (b) XRD patterns of exfoliated HNb_3O_8 nanosheet samples.

In order to understand such a difference in catalytic performance, activity tests were conducted over NS NBA (L) with less K^+ ions (prepared by HCl treatment). The resulting samples exhibited an activity decline in repeated runs, which implies that the catalyst durability is linked to residual K^+ ions in HNb_3O_8 nanosheet. Thus, we searched for a fingerprint for the presence of K^+ ions in the nanosheet materials. As a result, small reflections of $K_8Nb_{18}O_{49}$ crystallite were detected in the XRD patterns of NS NBA (S) and (L), but not in those of NS Nb_2O_5 (S) and (L). TEM-EDS analysis additionally revealed a little presence of K^+ in NS NBA (S) and (L), where the K/Nb atomic ratio was around 0.003. Therefore, it is believed that these potassium ions, even if small, would be displaced in between the layers of HNb_3O_8 nanosheet derived from amorphous NBA and that NS NBA (S) and (L) with more stacking are relatively durable in the reaction compared to NS Nb_2O_5 (S) and (L), respectively.

Then, we tried to figure out a possible reason for the above results. The strong evidence was found in layered KNb_3O_8; the K/Nb atomic ratio was approximately 1.5 times higher in NBA-derived materials than in Nb_2O_5-derived ones. This means that more intercalation of K^+ ions is achieved by using amorphous niobic acid as Nb source for KNb_3O_8, which is explained by more facile diffusion of K+ in the amorphous structure compared to the crystalline one.

4. Conclusions

Our work demonstrated that the property, activity and stability of HNb_3O_8 nanosheet are associated with how well K^+ ions are infiltrated in the step for the mixing of K and Nb sources. Compared to crystalline Nb_2O_5, niobic acid is structurally amorphous so that K^+ ions can penetrate well into more inside of the particles. Due to this effect, complete proton exchange would be difficult in NBA-derived HNb_3O_8 layers, thus a small amount of K^+ ions being present in the final nanosheet. These residual K^+ ions made HNb_3O_8 to consist of more layer stacking, consequently showing better catalyst durability in the dehydration reaction. This report would pave the way toward the preparation of catalytically active and stable HNb_3O_8 nanosheet.

References

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