

Facile Preparation of HNb_3O_8 Nanosheet with More Acid Sites

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Acid catalysts have been extensively studied in alcohol dehydration and much effort is paid to new catalyst development for highly efficient acid sites. There are two approaches for the preparation: one is to enhance acid site strength and the other is to increase the quantity of acid sites. In this work we intended to adjust the acid site quantity for layered (i.e., sheet-type) acid catalysts. For this purpose niobate nanosheet ($\text{e-HNb}_3\text{O}_8$) was selected because the synthesis protocol is well defined in literature [1]. Typically, the first step is solid-state reaction of K_2CO_3 and Nb_2O_5 in a molar quantity close to 1:3. Then, the solid mixture was calcined above 1000 °C, followed by ion exchange in a concentrated HNO_3 solution and subsequent exfoliation by tetraalkylammonium hydroxide (e.g., TBAOH). When the efficiency of each step was examined in a preliminary work, we found that the first solid-state reaction is a key step for affecting the final exfoliation step and thereby enhancing the product yield of $\text{e-HNb}_3\text{O}_8$ materials.

In the solid-state reaction such that K_2CO_3 was mixed with Nb_2O_5 in a mortar for a prolonged time, some portions of K^+ or CO_3^{2-} ion diffuse into the lattice of Nb_2O_5 solid. Thus, aqueous K_2CO_3 solutions of different concentration were contacted with Nb_2O_5 in order to increase the amount of diffused ions. The following steps were identical in all samples. The final catalysts were labelled as $\text{e-HNb}_3\text{O}_8\text{-L}_x$ where x is 100, 200 or 400. For comparison, the sample was also prepared by the solid-state reaction ($\text{e-HNb}_3\text{O}_8\text{-SS}$).

Interestingly, the product yield increased with the H_2O volume: based on the initial weight of Nb_2O_5 , the final recovery efficiency

was 25.5%, 64.9%, 72.4% and 88.1% for $\text{e-HNb}_3\text{O}_8\text{-SS}$, $\text{e-HNb}_3\text{O}_8\text{-L100}$, $\text{e-HNb}_3\text{O}_8\text{-L200}$ and $\text{e-HNb}_3\text{O}_8\text{-L400}$, respectively. It could be assumed from this result that $\text{e-HNb}_3\text{O}_8\text{-L400}$ shows a larger specific surface area, more acid sites exposed to the reactant, and consequently a higher catalytic activity. Our presumption is confirmed by the catalytic results, BET surface area and pyridine-chemisorbed FT-IR spectra, which are summarized in Table 1.

Table 1. Results of the prepared HNb_3O_8 nanosheet samples

	$\text{e-HNb}_3\text{O}_8\text{-SS}$	$\text{e-HNb}_3\text{O}_8\text{-L100}$
Conversion of 2-heptanol (mol%)	9.2	69.3
BET surface area ($\text{m}^2 \text{g}^{-1}$)	11	41
Acid amount (mmol g^{-1})	21.2	45.3
	$\text{e-HNb}_3\text{O}_8\text{-L200}$	$\text{e-HNb}_3\text{O}_8\text{-L400}$
Conversion of 2-heptanol (mol%)	72.4	74.1
BET surface area ($\text{m}^2 \text{g}^{-1}$)	47	53
Acid amount (mmol g^{-1})	48.7	51.5

From this data, we believe that the concentration of K_2CO_3 affects the efficiency of the exfoliation step. This will be caused by the infiltration degree of K^+ or CO_3^{2-} ion into the Nb_2O_5 lattice. Thus, the ball-milled samples prepared in this work have been characterized by PXRD and TGA-MS. The shifts of Nb_2O_5 reflections and CO_2 emission temperature reveal that more K^+ and/or CO_3^{2-} ion exist inside the lattice when a less concentrated solution is used. Consequently, our preparation method is facile and convenient for producing HNb_3O_8 nanosheet at a higher yield and with higher accessible acid sites and, in turn, enhanced activity in alcohol dehydration reactions.

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