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Characterization of $HNbMoO_6$, $HNbWO_6$ and $HTiNbO_5$ as solid acids and their catalytic properties for esterification reaction

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ABSTRACT

$HTiNbO_5$, $HNbMoO_6 \cdot H_2O$ and $HNbWO_6 \cdot 1.5H_2O$ were prepared by proton-exchange of the precursors $KTiNbO_5$, $LiNbMoO_6$ and $LiNbWO_6$, respectively, which were synthesized by a solid-state reaction method. The morphology and the micro-structure were characterized by means of scanning electron microscope (SEM), transmission electron microscope (TEM), powder X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FT-IR). NH_3 temperature-programmed desorption (NH_3-TPD) was used to measure the acidic properties of the samples. The Sanderson electronegativity and Kataoka's bond strength theory were also applied to investigate the acid properties of the as-prepared samples. Finally, their catalytic activities were evaluated through catalyzing the liquid-phase esterification reaction of acetic acid and *n*-butanol to form n-butyl acetate. It has been revealed that H^+ ions existed in different forms and interaction modes with M—O bond in the solid acids. The acid strength for these as-prepared samples follows the order $HNbMoO_6 \cdot H_2O > HNbWO_6 \cdot 1.5H_2O > HTiNbO_5$. In this work, $HNbMoO_6 \cdot H_2O$ presents an excellent catalytic activity for the esterification reaction, while $HNbWO_6 \cdot 1.5H_2O$ and $HTiNbO_5$ have little catalytic activity. The result suggested that the catalytic activity of the layered solid acid for the esterification reaction was mainly controlled by gallery height.

1. Introduction

Growing concerns regarding environmental and human health issues have necessitated the development of new industrial reactions with minimal environmental impact. Solid acid catalyst has drawn more and more attentions because of several advantages, such as no corrosion to equipment, environmental-friendliness and easy separation from reactants [1–5]. As a kind of solid acid material, proton-exchanged form of layered transition metal oxide possesses the merits of strong acidity, the adjustable surface properties and interlayer channel, the high surface area and excellent selectivity for the reactant molecules [6–19]. Niobium can combine with neighboring elements to form the layered compounds due to the good affinity. Recently, niobate has shown promising application in some water-containing reactions, such as dehydration, condensation and hydrolysis [20,21]. It has been reported that $HNbMoO_6$ has good catalytic activity for the reactions of Friedel–Crafts alkylation, esterification, condensation, hydration and hydrolysis [2,10,20–24]. Due to strong acid sites presenting in the interlayer, the catalytic activity of $HNbMoO_6$ is significantly higher than the molecular sieve and niobate in the process of esterification and hydrolysis. The difference of the interlayer proton activity and the laminate negative charges make the layered solid acids have the shape-selectivity for different reactants. In addition, the catalytic activity would change significantly if the reactants vary during esterification reaction process [18]. By exfoliation and aggregation of the nanosheets which made up of the layered material, the catalytic activity of the layered transition metal oxides can be improved dramatically [25]. For example, the layered $HTiNbO_5$ shows high catalytic activity on esterification, cumene cracking and isopropanol dehydration reactions after exfoliation and aggregation of the nanosheets [26–28]. Though the acidic characteristic and the formation mechanism of $HTiNbO_5$, $HNbMoO_6 \cdot H_2O$ and $HNbWO_6 \cdot 1.5H_2O$ have been explored detailedly [28], the influence of the composition, structure and bonding configurations of H^+ ions on the acidic characteristics still need to be explored from the theory.

Herein, the layered transition metal oxides $HTiNbO_5$, $HNbMoO_6 \cdot H_2O$ and $HNbWO_6 \cdot 1.5H_2O$ were obtained with a simple proton-exchange reaction. After discussion of the acid characteristics according to the Sanderson electronegativity and Kataoka's theory, the as-prepared solid acids were used to catalyze the esterification reaction of acetic acid and *n*-butanol. Under the same conditions, the catalytic activity of these three kinds of solid acids were investigated and compared carefully. On the other hand, the effect of the composition, structure and acidic characteristics of the as-prepared materials on the catalytic activity for the esterification reaction was studied specially.

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2. Experimental

2.1. Preparation of solid acids

Layered $HTiNbO_5$, $HNbMoO_6$ and $HNbWO_6$ were prepared by proton-exchange of the precursors $KTiNbO_5$, $LiNbMoO_6$ and $LiNbWO_6$, respectively, which were synthesized through a solid-state reaction method. The detailed procedure has been described as follows:

$KTiNbO_5$ was synthesized by heating a stoichiometric mixture of Nb_2O_5, K_2CO_3 and TiO_2 in Alumina crucible at 1373 K for 24 h with the heating rate at 5 K min^{-1}. Considering the volatilization of potassium, 15% excessive potassium carbonate was needed. Before calcining, this mixture was ultrasonicated at ambient temperature for 30 min. The precursor was washed with distilled water to remove the excess carbonate, and dried in air at 373 K for 10 h. The protonated form $HTiNbO_5$ was obtained by the treatment of $KTiNbO_5$ with 2 M HNO_3 at 323 K for 48 h under continuous stirring, with the one intermediate replacement of the HNO_3. Then the product was washed with distilled water and dried in air at 353 K over night.

The host $LiNbMoO_6$/$LiNbWO_6$ was synthesized by calcining the mixture of the stoichiometric Li_2CO_3, Nb_2O_5 and MoO_3/WO_3 at 853 K/1033 K for 24 h/72 h, respectively. The proton-exchange reaction was performed by shaking 2.0 g of $LiNbMoO_6$/$LiNbWO_6$ power in 40 mL of 2 M HNO_3 aqueous solution at 323 K for four days, exchanging the acid solution every 24 h over that period. Finally, the products were washed with distilled water and dried in air at 353 K over night.

2.2. Characterization

The X-ray diffraction (XRD) patterns were collected using a XD-3 powder diffractometer (Beijing Purkinje General Instrument Co., Ltd.) with a curved graphite-monochromatied CuKα radiation (λ = 1.5418 Å) operated at 40 kV and 30 mA under room temperature. The TEM microphotographies and SEM images were obtained by a Hitachi TM-1000 scanning electron microscope (SEM) (KYKY Technology Development Ltd.) with an acceleration voltage of 25 kV and a JEOL 2010 transmission electron microscopy (HRTEM) (JEOL Ltd.) with an acceleration voltage of 200 kV, respectively. The FT-IR absorption spectra were acquired on a Bruker Vector 33 FT-IR spectrophotometer (DTGS detector) with a resolution of 4 cm^{-1}.

The NH_3-TPD experiments were carried out using a continuous flow fixed-bed reactor system with thermal conduction detector (TCD, Tianjin Xianquan, Industry & Trade Development Co., Ltd.). Before NH_3-TPD experiment, 100 mg of the sample was placed in a quartz tube and heated at 453 K in a flow of N_2 (30 mL min^{-1}, 99.999%) for 1 h. The catalyst was cooled to 333 K and then NH_3 adsorption was performed by pulsing NH_3 to the sample until it was saturated. Then the sample was purged using N_2 (30 mL min^{-1}, 99.999%) to remove excessive NH_3 which came from the physically adsorption on the surface of catalyst. Finally, the NH_3-TPD profile was recorded in a flow of N_2 (30 mL min^{-1}, 99.999%) and the temperature was raised from 333 K to 973 K at a rate of 10 K min^{-1}.

2.3. Catalytic experiment

The catalytic activities of the samples were evaluated by the esterification reaction of acetic acid and *n*-butanol, which was performed in the flask equipped with a thermometer, a water separator and a reflux device. After putting 0.4 g catalyst, 104 mmol *n*-butanol and 80 mmol acetic acid in the flask, the mixture was maintained at 387 K until no water evaporated out. Then the separation was performed for removing the catalyst from the mixture after cooling. 0.1 M NaOH aqueous solution was used to titrate the acid in the mixture before and after the reaction, the consumed volume of NaOH aqueous solution was represented with V_1 and V_2, respectively. The esterification yield is equal to $(1 - V_2/V_1) \times 100\%$.

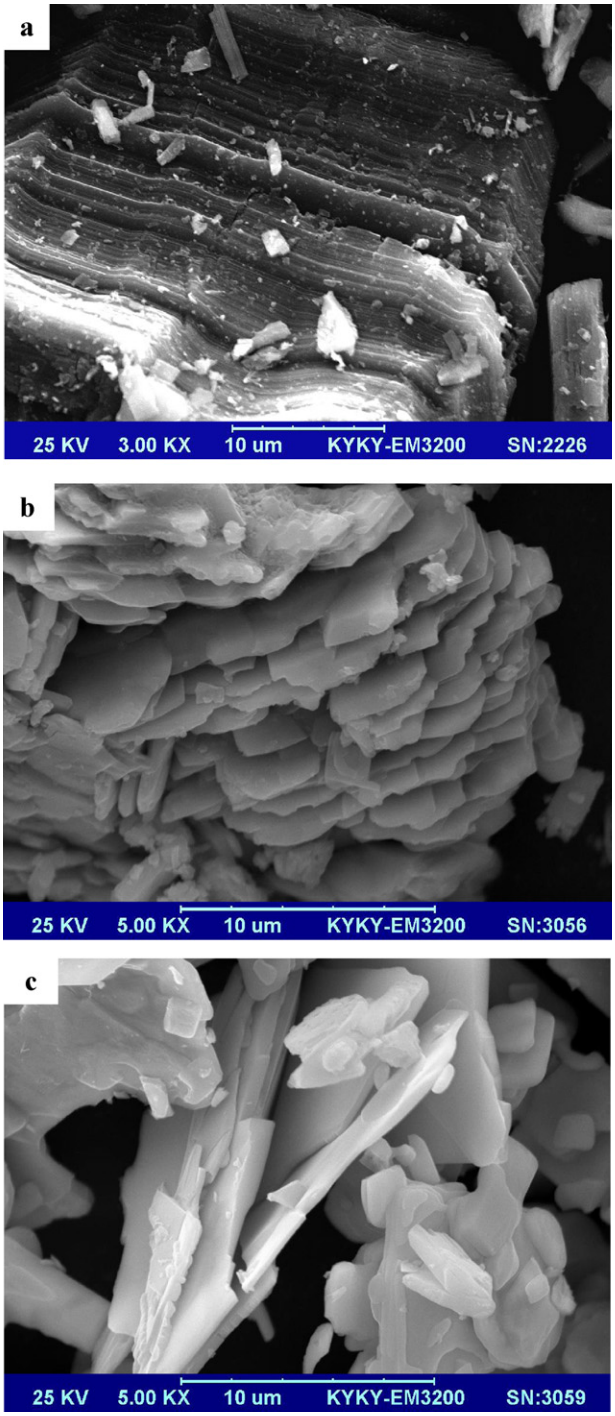

Fig. 1. SEM images of the as-prepared samples: (a) $KTiNbO_5$, (b) $LiNbMoO_6$ and (c) $LiNbWO_6$.

3. Results

3.1. Morphology and structure

The SEM images of $KTiNbO_5$, $LiNbWO_6$ and $LiNbMoO_6$ are shown in Fig. 1. As shown in Fig. 1, one can find that all these three layered metal oxides were made up of tabular particles with the size