Layered niobic acid with self-exfoliatable nanosheets and adjustable acidity for catalytic hydration of ethylene oxide

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ABSTRACT

Layered niobic acids ($H_xK_{1-x}Nb_3O_8$, $x = 0$–1) are reported as new solid acid catalysts for the selective hydration of ethylene oxide (EO). They are prepared by simply calcinating Nb_2O_5–K_2CO_3 mixture followed by an ion-exchange process in HNO_3 solution of different concentrations. The highest selectivity for monoethylene glycol (MEG) is achieved over 95% with EO conversion of >99% at x of 0.7 under H_2O/EO ratio of 8. Combined with the results of first-principles density functional theory calculations and Hammett indicator method, it is revealed that the suitable acid strength is more crucial for MEG selectivity than acid amount. Furthermore, a self-exfoliation of layered HNb_3O_8 is also found during EO hydration, which proves to be another important factor for its good catalytic performance by exposing the abundant acid sites among the $Nb_3O_8^-$ nanosheets. The thermal stability investigation of HNb_3O_8 also indicates a careful selection of characterization and application way for this layered niobic acid.

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1. Introduction

As an adaptable intermediate, monoethylene glycol (MEG) has found its increasing importance, particularly in the fabrication of polyester fiber. Up to now, catalytic hydration of ethylene oxide (EO) is still a predominant MEG preparation approach. However, a large excess of water (normally H_2O/EO > 20) has to be adopted to compress the production of by-products, causing enormous energy consumption during the distillation process. To improve the MEG selectivity at a relative low H_2O/EO ratio, considerable efforts have been made to explore efficient catalysts such as anion-exchange resins [1–3], supported metal oxides and zeolites [4,5], soluble inorganic salts [6], quaternary phosphoniumhalides [7], polymeric organosilane ammonium salts [8]. However, some apparent drawbacks still exist during the application of these catalysts, such as the swelling of resin, the separation of the catalysts from homogeneous system, and the complexity/high cost for the synthesis of some new catalysts.

Cation-exchangeable layered transition metal oxides are one of the attractive solid acid catalysts due to their enriched ion-exchangeable sites within the interlayer space. The layered metal oxide of $HNbMoO_6 \cdot nH_2O$ and $HTaMoO_6$ were reported as favorable acid catalysts for various reactions [9–11]. As an important type of solid catalyst, niobic acid (e.g., $Nb_2O_5 \cdot nH_2O$) has attracted much

attention in dehydration, hydration, esterification, hydrolysis, condensation, and alkylation reactions [4,12–17] for its unique acidity in presence of water. Recently, a lot of efforts are continuously focused on the catalytic application of layered niobic acids because of their nanosheet crystal structure and facile preparation via simply ion exchange of protons from their corresponding potassium niobates [18,19]. However, these solid catalysts are usually proved ineffective because the small d-spacing between their two-dimensional (2D) anionic nanosheets with high charge density prevents the penetration of the reactants into the interlayer region. Although the preparation of exfoliated sheets of layered niobic acids via soft-solution pre-exfoliation can overcome the above barrier [15,20–22], it still seems difficult in practical application because of the adoption of expensive agent (e.g., tetrabutylammonium hydroxide, TBAOH) during the redundant exfoliation process. In our present study, layered HNb_3O_8 is found to be capable of in situ self-exfoliation in some aqueous catalytic systems, and it is also reasonable to expect a remarkable catalytic activity of this material compared with pre-exfoliated samples.

On the basis of this discovery, herein, we report the first example of the layered $H_xK_{1-x}Nb_3O_8$ as the solid acid catalyst for EO hydration. The exchange degree value (x) can be precisely adjusted by carefully controlling ion-exchange conditions. The acidities of $H_xK_{1-x}Nb_3O_8$ catalysts are systematically characterized by theoretical calculation and Hammett indicator method. It is revealed that a moderate acid strength and the in situ self-exfoliation of $H_xK_{1-x}Nb_3O_8$ sheets are crucial for high MEG selectivity besides

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the acid amount, and the highest MEG selectivity is achieved over 95% with EO conversion of >99% at x of 0.7. This result is consistent with that in our previous report for the soluble salts/acids catalysts [6], which demonstrated that the best MEG selectivity is achieved within the mild pH range of 3.0–6.0. The conclusions drawn in this work not only considerably inspire the exploitation of new catalyst for EO hydration but are also beneficial for the further understanding of acidic nature, exfoliation effect, and catalytic properties of layered niobic acid. More importantly, the validity of the theoretical calculation on the prediction of acid strength can be proved as well.

2. Experimental

2.1. Preparation of niobic acid catalyst

The chemicals used in the present work including Nb_2O_5, K_2CO_3, HNO_3, ethylene oxide, TBAOH (25%), and deionized water were commercially purchased and used without further purification.

KNb_3O_8 was prepared by molten salt method from a finely grinded mixture of Nb_2O_5 and K_2CO_3 with a slightly excessive amount (10%) of K_2CO_3 to the stoichiometric ratio. The calcination was held at 900 °C for 1 h and then at 1100 °C for 5 h. The KNb_3O_8 product obtained was then washed with hot water to remove the residual K_2CO_3. The phase purity was confirmed by X-ray diffraction (XRD). KNb_3O_8 was then used as the precursor to prepare $H_xK_{1-x}Nb_3O_8$ by a proton-exchange method [23,24]. KNb_3O_8 sample was stirred in a series of HNO_3 solutions with different concentrations (0.2, 2.2, 3.8, 6.5, 10, 20, and 40 wt%) at solution/solid weight ratio of 60 for 48 h to produce $H_xK_{1-x}Nb_3O_8$ with x of 0.11, 0.31, 0.35, 0.49, 0.71, 0.76, and 0.89, respectively. The x values were measured by inductively coupled plasma atomic absorption spectrometry (ICP-AAS). Besides, a fully proton-exchanged sample (HNb_3O_8) was prepared by treating KNb_3O_8 repeatedly in 40 wt% HNO_3 solutions for three times (72 h for each run) at ambient temperature.

The comparative pre-exfoliated HNb_3O_8 was also conducted in TBAOH aqueous solution as reported in previous work [20]. The other two niobic acids of $HNbO_3$ and $H_4Nb_6O_{17}$ were prepared by the similar molten salt synthesis method but with different amount of K_2CO_3 [25,26], followed by repeated acid-exchange treatments.

2.2. Characterization

Scanning electron microscopy (SEM) measurements were performed by a Philips XL30 D6716 instrument at an operating voltage of 25 kV, while transmission electron microscopy (TEM) experiments with selected area electron diffraction (SAED) were carried out with a JEOL JEM-2010 instrument at an operating voltage of 200 kV. XRD patterns were recorded on a Rigaku D/Max-rB 12 kW diffractometer (Cu Kα). N_2 sorption isotherms were recorded with a Micromeritics ASAP 2010 instrument at 77 K. The potassium content in the acid-exchange solution was determined by ICP-AAS (Zeeman-5000). Fourier-transform infrared (FT-IR) spectra were collected on a Nicolet Fourier Spectrophotometer-360 using KBr pellets. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA-SDTA851 analyzer from 25 to 900 °C under nitrogen with ramp of 5 °C/min.

2.3. Acid strength H_0 determination by Hammett indicator method

The Hammett indicators used were neutral red, methyl red, 4-dimethylamino-azobenzene, crystal violet, and anthraquinone with the pK_a values of +6.8, +4.8, +3.3, +0.8, and −5.6, respectively. The indicators were resolved in dried petroleum ether of reagent grade and its concentration was 0.1 wt% [27]. After drying in vacuum, 100 mg of grinded sample was rapidly transferred into a transparent tube and 2 ml of petroleum ether was injected to cover the sample. Subsequently, several drops of indicator solution were added followed by vigorous shaking. The range of H_0 value was determined by color variation.

2.4. Methodology and theoretical calculation details for acid strength (pK_a)

The acid strength value pK_a of $H_xK_{1-x}Nb_3O_8$ was calculated using the SIESTA package [28] with numerical atomic orbital basis sets [29] and Troullier–Martins norm-conserving pseudopotentials [30]. The exchange–correlation function utilized was GGA-PBE, and the double-ζ plus polarization (DZP) basis set was employed. The semicore 4s and 4p states of Nb were included. The cutoff for the real space grid was set as 150 Ry. The quasi-Newton BFGS method was employed for geometry relaxation until the maximal forces on each relaxed atom were less than 0.1 eV/Å. The solvation energy due to the long-range electrostatic interaction was computed by a periodic continuum solvation model with a smooth dielectric function. The detailed algorithm of the continuum solvation method has been addressed by Fattebert and Gygi [31], which has been implemented by us for the calculations of solvation energies of free molecules and for periodic system previously [32,33]. A large vacuum region (30 Å) along Z-axis that separates two adjacent sheets was introduced. In solving the Poisson–Boltzmann equation numerically, we utilized a sixth-order FD scheme that is appropriate to discretize partial differential equations with periodic boundary conditions [34]. This scheme utilizes the finite-difference stencil to get the symmetric sparse linear system. In terms of the symmetry, the linear system is solved iteratively by a parallel version of MINRES with the preconditioner. To realize a fully parallelism, we chose the incomplete LU preconditioners based on the second-order FD scheme in a localized preconditioner implementation.

The pK_a of the solid acid was calculated by:

$$pK_a = \frac{\Delta G_{diss}}{2.303 k_B T} - 1.74 = 16.88 \Delta G_{diss} - 1.74 \tag{1}$$

where −1.74 is the pK_a of H_3O^+, and ΔG_{diss} is the Gibbs free energy of dissociation:

$$AH + H_2O \rightarrow A^- + H_3O^+ \tag{2}$$

$$\begin{aligned}
\Delta G_{diss} &= G(A^-) - G(AH) + G(H_3O^+) - G(H_2O) \\
&= E(A^- - AH) + ZPE(A^- - AH) + G(H_3O^+ - H_2O) \\
&= E(A^- - AH) - 0.27eV - 11.53eV \\
&= E(A^- - AH) - 11.80eV
\end{aligned} \tag{3}$$

where −11.53 eV is the free energy difference value between H_3O^+ and H_2O [35].

2.5. Catalytic testing

The hydration reaction of EO was carried out in an isothermal batch autoclave reactor with a typical H_2O/EO molar ratio of 8 under continuous stirring (200 rpm) at 110 °C, and the pressure was kept as 1.5 MPa by N_2. The catalyst amount is normally 3 mmol/mol EO. After a 0.5-h reaction, the reactor was cooled down and the products were analyzed on a GC920 gas chromatograph equipped with a HP-INNOWAX column and a flame ionization detector. Since EO conversion with any catalyst was nearly 100%, MEG selectivity was chiefly taken into account as the criterion