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Exfoliated Pd/HNb_3O_8 nanosheet as highly efficient bifunctional catalyst for one-pot cascade reaction

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ABSTRACT

Ultrathin two-dimensional metal oxide nanosheets have drawn attention as potential solid acid catalysts owing to their strong acidity, attributed to the bridged OH groups formed on the nanosheets. In this study, a new class of bifunctional acid–metal catalyst was realized by the deposition of Pd on layered niobium oxide (KNb_3O_8 and HNb_3O_8) or its exfoliated nanosheet (Pd/HNb_3O_8-NS) and applied to one-pot cascade deacetalization and hydrogenation. It was found that the acid strength of the support exerted a large influence not only on the promotion of the first deacetalization step, but also on the acceleration of the subsequent hydrogenation step. Comparative experiments using a series of Pd/HZSM-5 catalysts with different acidities reconfirmed the crucial role of acid strength on hydrogenation. However, the superior catalytic activity of Pd/HNb_3O_8-NS for hydrogenation compared to that of Pd/HZSM-5 of similar acidity suggests a more efficient ensemble effect of the strong acid sites with the nearby metal sites on the nanosheet surface. Among the catalysts used, Pd/HNb_3O_8-NS showed the best catalytic performance for one-pot cascade reaction affording the desired product (benzyl alcohol) in approximately 92% yield, which was 7.1 and 1.2 times higher than that of layered Pd/KNb_3O_8 or Pd/HNb_3O_8, respectively. The excellent catalytic performance of Pd/HNb_3O_8-NS may result from the characteristic features of nanosheets: (i) the synergistic cooperation between the bifunctional active sites and (ii) the two-dimensional open surface offering easier access of the reactants to the active sites. Although the use of $NaBH_4$ as hydrogen source was effective in improving the initial reaction performance, the basic nature of $NaBH_4$ adversely resulted in weakening the acid strength of the catalyst, and consequently led to a reduction in catalytic activity.

1. Introduction

Conventionally, large amounts of useful chemicals are produced through a number of chemical transformations and the demand for time and resources for purification, as well as production, may increase as the molecular complexity increases. Since multistep processes for chemical production are clearly undesirable in terms of process efficiency, the design of an efficient cascade or tandem catalyst closely mimicking nature's multistep reaction cascades is one of the most fascinating but elusive challenges in the field of catalyst research [1–4].

To realize an elegant catalyst design for certain one-pot cascade reactions, it is of prime importance that the different active sites in a single system not only catalyze the multistep chemical transformations in a cascade manner, but also do not negatively affect each other. Moreover, it is preferable that they act synergistically to increase catalytic efficiency. Although several homogeneous catalysts combining different chemical functions have been proposed [5,6], heterogeneous catalysts in principle appear to offer better opportunities for achieving high efficiencies in cascade reactions by providing more effective site isolation of different functions in a single system [7–11].

In this context, a range of heterogeneous multifunctional catalysts, i.e., Brønsted acid–Lewis acid, acid–base, acid–metal, and base–metal systems, have recently been extensively investigated. Two types of Brønsted acid–Lewis acid bifunctional catalysts can be prepared by either simultaneous incorporation of both Brønsted and Lewis acid sites in the structure of molecular sieves, or the use of a physical mixture of Brønsted and Lewis acids [12,13]. For acid–base bifunctional catalysts, the difficulty lies in the efficient isolation of the antagonistic acid–base sites on the same support, and therefore sophisticated structures such as core–shell nanoreactors [14,15], Pickering emulsion droplets [16], or site-isolated acid–base bifunctional metal–organic frameworks [17] were envisaged to solve this challenging problem. Acid–metal bifunctional catalysts have been widely used in the fine chemical as well as

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petrochemical industry [4,18]. They are usually prepared by classical metal impregnation on acidic supports. Among the acidic supports, well-ordered micro- and mesoporous molecular sieves have been popular because they may offer a relatively easy selection of acid types (Brønsted, Lewis, or Brønsted/Lewis) and render fine tuning of the acid strength by changing their composition, such as SiO_2 to Al_2O_3 ratio [19,20]. In the case of a cascade reaction over a base–metal bifunctional catalyst, the metal sites generally act as hydrogenation functions and the base sites on the metal oxide supports undertake the promotion of the condensation of aldehydes or ketones [21,22].

From the viewpoint of achieving highly efficient one-pot cascade reactions, it is worth noting that the important consideration for the design of acid– or base–metal bifunctional catalysts is different from that for an acid–base system. Because interactions between acid and base sites may reduce the acidity and/or basicity, well-defined site isolation is critical for the preparation of acid–base bifunctional catalysts, to suppress unfavorable neutralizing effects between the antagonistic active sites. In the case of acid– or base–metal bifunctional catalysts, on the other hand, ensemble or synergistic catalysis of the metal site with the acid or base site is advantageous for accelerating the reaction rate or improving the selectivity for a desired product. There have been examples showing that the surface properties of supports play important roles in determining the catalytic performance [23–28].

In the meantime, ion-exchangeable layered metal oxides offer several attractive features owing to their wide variety of structural and electronic properties [29]. However, few examples of catalytic applications of layered metal oxides have been reported because access of the reactant molecules to the active site is rather difficult due to the highly charged nature of the layered sheets [30]. To overcome the resistance to intercalation, exfoliation of the layered sheet has been extensively studied and it has been found that the two-dimensional structure of the nanosheets is a prerequisite for significantly reducing the diffusion problems [29–31]. In addition, the formation of acidic hydroxyl groups on the exfoliated nanosheets makes it possible to use them as efficient solid acid catalysts. A range of metal oxide nanosheet catalysts, such as $HTiNbO_5$, $HNbWO_6$, $HNbMoO_6$, $HTaWO_6$, HNb_3O_8, and $Nb_2O_5{\cdot}nH_2O$ has been applied for Friedel–Crafts alkylation, esterification, hydrolysis, and dehydration [32–36]. Recently, promising photocatalytic activities of niobate nanosheets for CO_2 conversion and hydrogen evolution reaction have also been reported [37–39]. Moreover, the unique properties of the metal oxide nanosheets make them one of the most promising candidates that can meet the need for a solid acid support material in heterogeneous catalysis: a high concentration of durable acid sites on an easily accessible open surface.

In the present study, a new class of bifunctional acid–metal catalyst was realized by the deposition of Pd on layered niobium oxide (KNb_3O_8 and HNb_3O_8) or its exfoliated nanosheet (Pd/HNb_3O_8-NS) and applied to one-pot cascade deacetalization and hydrogenation, as described in Fig. 1. To the best of our knowledge, this study is the first successful application of a metal-supported exfoliated nanosheet catalyst for a one-pot cascade reaction.

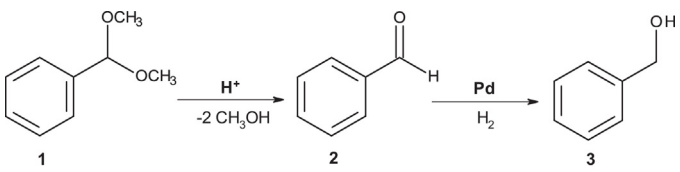

Fig. 1. Reaction scheme for one-pot cascade reaction; benzaldehyde dimethyl acetal (**1**), benzaldehyde (**2**), and benzyl alcohol (**3**).

2. Experimental

2.1. Chemicals

Potassium carbonate (K_2CO_3, 99.5%) and niobium oxide (Nb_2O_5, 99.9%) was supplied from Junsei (Japan). Tetrabutylammonium hydroxide (TBAOH, 40 wt%), sodium borohydride ($NaBH_4$, 98%), palladium acetate ($Pd(OAc)_2$, 98%), benzaldehyde dimethyl acetal (99%), benzaldehyde (99%), and benzyl alcohol (>99%) were purchased from Aldrich. A series of ammonium form ZSM-5 zeolites with different SiO_2/Al_2O_3 ratios were obtained from Zeolyst. Before use, the zeolites were calcined at 673 K for 4 h. Nitric acid (60 wt%), toluene (99.5%), and ethanol (>99.5%) were obtained from Samchun (Korea). All chemicals except for zeolites were used as received without further purification.

2.2. Catalyst preparation

Layered KNb_3O_8 was prepared by conventional solid state reaction following to the methods reported elsewhere [40,41]. Stoichiometric amounts of Nb_2O_5 and K_2CO_3 were well milled for 24 h and then heated at 1373 K for 5 h. Considering the volatilization of potassium, 10% excessive K_2CO_3 was added. The sample was washed with distilled water to remove the excess carbonate after calcination. The proton-exchange of KNb_3O_8 was performed by shaking 5 g of KNb_3O_8 in 2 M nitric acid solution at room temperature for 3 days. The acid solution was renewed each day in order to ensure full exchange of alkali ions. After completion of the ion-exchange, the HNb_3O_8 product was washed thoroughly with distilled water and dried in air at 373 K. Exfoliation of the layered HNb_3O_8 to the corresponding nanosheet was carried out by the insertion of voluminous and hydrophilic cations to expand the interlayer spaces of the layered structures. For this, 15 wt% TBAOH solution was mixed with 150 mL of distilled water containing 3.0 g of HNb_3O_8. In a typical reaction, TBAOH solution was added to the suspension until the pH reached 10.5, and the resultant solution was shaken for 3 days. After then, random aggregation of the nanosheets was obtained as a precipitate form by the addition of aqueous nitric acid solution (0.1 M, 20 mL) to the resulting exfoliated suspension. The aggregated sample was centrifuged, washed with 0.1 M HNO_3 twice, and then washed thoroughly with distilled water to remove residual HNO_3.

A series of Pd supported niobium oxide catalysts were prepared using an alcohol-reduction method in ethanol; $Pd(OAc)_2$ (5 mg), ethanol (20 ml), and support (1 g) was added to a 50 ml beaker and the mixture was stirred at room temperature for 24 h. Then the solid was recovered by filtration and washed with ethanol three times, and dried *in vacuo* at 393 K for 12 h. A series of Pd/HZSM-5 catalysts were prepared in a similar manner.

2.3. Catalyst characterization

X-ray powder diffraction (XRD) analysis was performed on a Rigaku diffractometer using CuKα ($\lambda = 1.54$ Å) radiation at 0.5° min^{-1}. The specific surface area and pore volume of the catalysts were determined by N_2 adsorption using a BELSORP-Max (BEL, Japan) at 77 K. Prior to adsorption, samples were degassed under vacuum conditions at 423 K overnight. Field emission scanning electron microscope (FE-SEM) was carried out using a Hitachi S-4800 with 10 kV accelerating voltage. Field-emission transmission electron microscopy (FE-TEM) was carried out using a Tecnai G2 F20 460 L transmission electron microscope. Ammonia temperature-programmed desorption profiles were obtained using a BEL-CAT chemisorption analyzer. Before ammonia adsorption, samples were activated in a helium flow of 100 ml/min at 373 K for 2 h. The samples were subsequently exposed to ammonia until