Utilization of hexagonal boron nitride as a solid acid–base bifunctional catalyst

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ABSTRACT

This work explores the use of hexagonal boron nitride (h-BN), a graphite-like compound, as a novel catalyst with base and acid functionalities. For use as a solid catalyst, the layered structure of h-BN was disrupted by ball-milling, exposing boron and nitrogen edge sites as well as increasing the surface area from 3 to ca. 400 $m^2 g^{-1}$. Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and proton magic-angle spinning nuclear magnetic resonance spectroscopy (^{1}H MAS NMR) indicated simultaneous and adjacent formation of amino and hydroxyl groups by milling, which function as Brønsted base and acid sites, respectively. Analysis using color indicator reagents and pyrrole-adsorbed ^{1}H MAS NMR results revealed that the ball-milled h-BN had basic sites of strength +9.3 > H$_-$ $\geq$ +7.2, comparable to those of KY zeolite. Measurements of ^{31}P MAS NMR of adsorbed trimethylphosphine oxide indicated that the ball-milled h-BN had weak acid sites, comparable to those in HY zeolite. Despite its weak basicity, the ball-milled h-BN showed high activity and selectivity toward β-nitroalkenes for the nitroaldol reaction (Henry reaction) and the Knoevenagel condensation, whereas nontreated h-BN did not show activity. The nitroaldol reaction was considered to proceed in two steps: the abstraction of a proton from nitromethane by the amino group and the formation of an imine followed by a nucleophilic attack of the deprotonated nitromethane. Kinetic isotope effect experiments using ᴅ-substituted nitromethane revealed that the first step was the rate-determining step. Several nitroaldol reactions using a variety of monosubstituted benzaldehydes indicated that electron-donating groups enhanced the activity, suggesting that the formation of adjacent base and acid sites is responsible for it. This study shows the high catalytic activity of BN, a solid catalyst with moderate basicity and weak acidity.

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1. Introduction

Design of well-defined catalytic active sites and understanding of their catalytic behavior are of significance for both homogenous and heterogeneous catalysts. The concept of frustrated Lewis pairs in which Lewis acid and base sites are rationally positioned in one molecule without neutralization is an excellent example of the application of homogeneous acid–base cooperative catalysts for the activation of small molecules, including hydrogen, alkynes, and carbon dioxide [1–3]. Another good example is the molecular catalyst proline, which is an amino acid consisting of a secondary amine-containing pyrrolidine with an attached carboxylic acid group [4]. The acid and base sites are appropriately positioned and efficiently catalyze asymmetric aldol reactions.

For heterogeneous acid–base catalysts, amine-tethered silica materials such as bulk silica [5], mesoporous silica [6–8], and silica-alumina [9] have been extensively studied as efficient acid–base cooperative catalysts that catalyze carbon–carbon bond formation reactions including aldol, nitroaldol, and Knoevenagel condensations and the Michael addition. For aminosilica materials, the coexistence of weak acid sites (e.g., silanols) with base sites (alkylamines) in spatially appropriate positions is a key to realizing high catalytic activity for these reactions. The neighboring weak acid sites are important because they help to stabilize the carbonyl groups of the ketone and aldehyde species, which efficiently promotes the condensation reactions. To maximize the cooperativity, there is an optimal distance between acid and base sites, which can be controlled by adequate concentration of acid and base sites [10], use of aminoalkyl silanes with appropriate alkyl linker lengths [11], and adjustment of pore size for mesoporous silica [8]. The spatial positioning of the acid–base pair with high precision is

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necessary, but the active pairs formed on silica are average structures because of the amorphous nature of the silica, in which a variety of surface silanols including isolated, vicinal, and geminal silanols with slightly different bond lengths are present [12,13].

An alternative method of developing acid–base pairs on silica is the use of strained siloxane bridges as a source of active pairs. Opening of siloxane bridges by base molecules simultaneously affords acid–base sites [14,15]. One example is ammonia treatment at low temperature of a mesoporous silica that was pretreated at high temperature [14]. The high-temperature calcination led to formation of strained siloxane bridges, Si—O—Si. Ammonia dissociatively adsorbed onto the siloxane bridges by the reaction –Si—O–Si– + NH_3 → -Si–NH_2 + –Si–OH. The thus formed acid–base pairs were well-defined and functioned as cooperative catalysts for the Knoevenagel condensation. Very recently, it was reported that mesoporous silica SBA15, which mostly has strained reactive siloxane rings, reacted with aniline to produce N-phenylsilanamine–silanol acid–base pairs, which were also effective for the Knoevenagel condensation. The SBA-15 was pretreated at very high temperature (1100 °C) under vacuum before reaction with aniline [15].

It is desirable to design such well-defined acid–base pairs for other materials composed of different elements. Utilization of the crystal structure of inorganic compounds is a promising approach. In this study, hexagonal boron nitride (h-BN) was investigated as a new bifunctional catalyst. h-BN is a layered compound isostructural with graphite and has been widely studied for diverse applications outside of catalysis, such as electronic and optical devices using heterostructures linked by van der Waals forces [16,17], coating materials with high-temperature oxidation resistance [18], adsorbents for organic compounds useful in water cleaning [19], and materials for hydrogen storage [20]. Unlike graphite, BN has unshared electron pairs localized on the nitrogen atoms, resulting in a polarized nature. Owing to strong chemical bonding between the atoms and physical bonding between the layers, BN is chemically and thermally stable, electrically insulating, and mechanically robust. However, very recently, h-BN was found to catalyze oxidative dehydrogenation of alkanes [21,22], and hydrogenation [23]. The present study focuses on the chemically polarized nature of h-BN. The nitrogen and boron composing h-BN are expected to function as base and acid sites, respectively, under appropriate treatment. A top-down ball-milling method was chosen to disrupt the structure of bulk h-BN [24–26], resulting in exposure of the edge sites of the planar h-BN. This study reveals that amino and hydroxyl groups were simultaneously formed at adjacent positions on the h-BN surface using the simple ball-milling method, and these groups functioned as efficient cooperative acid–base sites for the nitroaldol reaction.

2. Experimental

2.1. Preparation of ball-milled h-BN

A quantity of 0.8 g of h-BN (Wako Pure Chemical Industries, Ltd.) was ball-milled at 400 rpm for 6–24 h using a planetary ball mill (Pulverisette 7, Fritsch, zirconia vessel with six zirconia balls (diameter 10 mm)). Ball milling was conducted for 12–48 cycles, in which each cycle was carried out for 30 min with 5 min intervals. The rotation direction was reversed each cycle. The samples prepared were denoted as h-BN bm6–24 h, respectively.

2.2. Characterization

The specific surface area of the catalysts was evaluated by the Brunauer–Emmett–Teller (BET) method using nitrogen adsorption (BELSORP-mini II, Microtrac-BEL). Samples were pretreated by evacuation at 200 °C for 3 h prior to the measurements.

The crystal structure of the catalysts was determined by X-ray diffraction (XRD) (RINT-2700, Rigaku with CuKα radiation) at a voltage of 40 kV and a current of 100 mA with 2θ values from 20° to 60°. Measurements were made on samples without pretreatment.

Fourier transform infrared spectroscopy (FTIR) (FT/IR-6100, JASCO) measurements were performed to identify functional groups on the catalysts. Samples without pretreatment were pressed into pellets with KBr for the measurements.

X-ray photoelectron spectroscopy (XPS) (JPS-9200, JEOL with MgKα radiation) measurements were carried out to investigate the oxidation state of elements and their compositions over the catalyst surface. The binding energies in each measurement were referenced to the core level of the C1s peak (284.8 eV), and all obtained peaks were fitted by Gaussian curves. The samples were not pretreated.

Titrations using color indicator reagents were carried out to evaluate the base strength and base amounts of the catalysts. A quantity of 50 mg of catalyst was added to 1 mL of toluene solution containing 0.4 mg of bromothymol blue (pK_a = 7.2) or phenolphthalein (pK_a = 9.3) for 1 day. The base amounts of the catalyst were determined by titration using 0.01 M benzoic acid in toluene.

Proton magic-angle spinning nuclear magnetic resonance (^{1}H MAS NMR) measurements were conducted to quantify proton-containing functional groups (hydroxyl and amino groups). Measurements were carried out as previously reported [27]. The ^{1}H MAS NMR spectra were recorded with a Bruker Avance III HD 600WD spectrometer operating at a frequency of 600.39 MHz. A Bruker MAS probehead was used with a zirconia rotor of outer diameter 4 mm. All measurements were performed at room temperature with a spinning rate of 10 kHz. The ^{1}H spectra were measured with an ordinary single pulse sequence. The flip angle of the pulse and the recycle delay were π/2 and 3 s, respectively. We did not measure the ^{31}P spin–lattice relaxation times of the present samples. The ^{31}P spin–lattice relaxation times are 6.3 and 1.7 s for crystalline and hydrated TMPO, respectively [28]. The ^{31}P spins are relaxed mainly by the rotation of the methyl group. We did not quantitate the adsorbed TMPO, and thus full recovery was not necessary. To improve the efficiency of the signal accumulation, we set the recycle delay to 3 s. The ^{1}H chemical shift was expressed with respect to neat tetramethylsilane (TMS). Experimentally, secondary standard compounds were used, such as adamantane (1.85 ppm at a spinning rate of 8 kHz). The ^{1}H content in the samples was quantitated by comparing the integrated signal intensities of the samples with that of adamantane.

The solid base properties of the catalyst were investigated by ^{1}H MAS NMR using pyrrole (Wako Pure Chemical Industries, Ltd.) as a probe molecule. In a typical adsorption experiment, an appropriate volume of pyrrole (2–10 μL, 0.03–0.14 mmol) was injected into a glass tube containing h-BN (0.20 g) under nitrogen. Samples were heated to 100 °C for 3 h to ensure homogeneous distribution of the probe molecules. Samples were carefully transferred into a zirconia rotor in nitrogen atmosphere and capped tightly to avoid moisture.

The solid acid properties of the catalysts were examined by ^{31}P MAS NMR using trimethylphosphine oxide (Wako Pure Chemical Industries, Ltd) as a probe molecule. The NMR spectra were measured at room temperature using a Bruker Avance 400 spectrometer at a Larmor frequency of 161.98 MHz. A single-pulse sequence was employed with high-power proton decoupling at a sample spinning rate of 8 kHz. The flip angle of the pulse and the recycle delay were π/4 and 3 s, respectively. The ^{31}P chemical shift was referenced to 85% H_3PO_4 at 0.0 ppm, with $(NH_4)_2HPO_4$ used as a secondary reference material at 1.33 ppm. The samples with adsorbed