Origin of the excellent catalytic activity of Pd loaded on ultra-stable Y zeolites in Suzuki–Miyaura reactions

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ABSTRACT

Suzuki–Miyaura reactions were performed over Pd loaded on (ultra-stable Y) USY zeolites prepared by steam treatment of NH_4–Y. We found that the catalytic activity of Pd increased significantly with steam treatment of NH_4–Y when 6% H_2 was applied before and during the reactions. For instance, a TON of 13,000,000 was obtained in the reaction between bromobenzene and phenylboronic acid in 1.5 h. Pd K-edge and Pd L_3-edge X-ray absorption fine structure analyses revealed the formation of atomic Pd with a cationic character. The catalytic activity of Pd/USY prepared under different steam-treatment conditions was in good correlation with the strong Brønsted acid sites induced by the extra-framework Al. Based on the catalytic performance data, the structure of Pd, and acidic analysis of the support, atomic Pd anchored to the strong Brønsted acid sites of the USY zeolite was proposed to be the active species.

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1. Introduction

Cross-coupling reactions, such as Suzuki–Miyaura and Mizoroki–Heck reactions, are important in the production of pharmaceuticals, organic electroluminescent devices, and liquid crystals [1–4]. Numerous Pd complexes, such as palladacycles [5] and *N*-heterocyclic carbine [6,7], have been developed for use in these reactions [8]. However, these Pd(0) or Pd(II) complexes cause difficulties in the synthesis and purification of the final product. Another class of catalysts for these reactions, namely heterogeneous catalysts, is easy to prepare and readily separated from the products. For this purpose, Pd has been supported on various materials, including active carbon [9], zeolites [10–13], double-layer hydroxides [14], modified silica [15–17], hydroxyapatite [18], and polymers such as dendrimers [19,20] and polyethylene glycol [21]. Among these supported catalysts, there are several reports on supported Pd catalysts that are nearly as active as the best homogeneous ones [13,14,22]. These highly active heterogeneous catalysts have been realized when well-dispersed active sites with a homogeneous structure are fabricated on supports. Moreover, well-dispersed metals having surface atoms with a low coordination number (CN) are anticipated to exhibit high activity; this behavior is different from that of a bulk-type catalyst. Zeolites have a large surface area and uniform micropores, which can accommodate dispersed metal clusters, leading to a high surface-to-volume ratio [23]. Using zeolites as supports for Pd is therefore expected to lead to high catalytic activity. Among the various zeolites, faujasite (FAU)-type zeolites are the most promising for use as a support for Pd because they have large supercage with diameters of ca. 1.3 nm. Indeed, we found that Pd loaded on ultra-stable Y (USY) zeolites exhibited excellent catalytic activity in a Suzuki–Miyaura reaction when H_2 was bubbled through the system prior to the reaction [24]. The reaction only took place when *o*-xylene and Pd ammine complexes were used as the solvent and the Pd precursor, respectively. The catalytic activity was improved significantly by continuously bubbling H_2 through the system during the reaction [22]. Pd K-edge extended X-ray absorption fine structure (EXAFS) analysis revealed the formation of atomic Pd species after H_2 bubbling in *o*-xylene. In addition to studying the active sites, it is important to obtain insights into the role of the support, taking into account that the catalytic performance of Pd varies significantly, depending on the type of support. Of particular interest is the USY zeolite, on which Pd exhibited extremely high activity in Suzuki–Miyaura reactions. However, little is known about the reason for the development of such a high activity in the Pd/USY catalyst. In general, USY zeolites are prepared by steam treatment of Y-type (FAU structure) zeolites ion exchanged with NH_4^+ cations (NH_4–Y) at temperatures of around 823 K [25]. The NH_4–Y steam treatment causes the formation of mesopores and the evolution of strong acid sites as a result of dealumination from the framework structure [26]. Tuning of the acid properties of USY is also possible by changing the steam-treatment conditions, i.e., temperature, time, and H_2O vapor concentration.

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Here, we focused on the strong acid sites present in USY, with the aim of obtaining insight into the genesis of active species in Pd/USY which showed excellent catalytic performance in Suzuki–Miyaura reactions that was not realized on other kinds of supports including H–Y, ZSM-5, Mordenite, Al_2O_3, and active carbon [22]. This is because acid sites of zeolites played an important role in the determination of the dispersion of Pd, as proved primarily by in situ X-ray absorption fine structure (XAFS) studies [27–29]. The IR spectroscopy/MS spectrometry-temperature programmed desorption (IRMS-TPD) method of adsorbed NH_3 was used to study the acid properties of USY zeolites prepared under different steam-treatment conditions in detail. In this method, IR and MS work together to follow the thermal behavior of adsorbed and desorbed NH_3, respectively [30]. Using this method, information on the number and strength of acid sites is obtained simultaneously. The obtained data were correlated with catalytic performance coupled with XAFS data. Such a combined study enabled us to reveal the origin of the extremely high activity of Pd/USY catalysts.

2. Experimental methods

2.1. Catalyst preparation

Na–Y zeolite (320NAA) supplied by the Tosoh Corp., Tokyo, Japan was employed as the starting material for the preparation of USY. The Na–Y was ion exchanged three times with a solution of NH_4NO_3 (0.5 mol L^{-1}) at 353 K to give NH_4–Y. USY was prepared from NH_4–Y zeolites by treatment with H_2O vapor diluted with an N_2 flow. Typical concentration of H_2O vapor was 18 vol.% with an exception of steaming with 40 vol.%-H_2O. NH_4–Y (5 g) was placed in a quartz tube and treated with H_2O vapor for 1–10 h at 673–873 K. The total flow rate was 50 mL min^{-1}. The obtained USY was ion exchanged three times with NH_4NO_3 (0.5 mol L^{-1}) at 353 K to give NH_4–USY. The completion of ion exchange of H^+ with NH_4^+ was confirmed by TPD of NH_3, showing that 93% of H^+ had been replaced with NH_4^+. The NH_4–USY was then heated to 573 K in air to partially remove NH_3. Pd was then introduced to the calcined USY by an ion-exchange method using $Pd(NH_3)_4Cl_2$ solution (3.8×10^{-4} mol dm^{-3}; Aldrich, St. Louis, MO, USA) at room temperature (r.t.) [31]. The suspension was washed with deionized H_2O and dried in an oven at 323 K overnight. The Pd loading of all samples was 0.4 wt.%, as measured by inductive coupled plasma (ICP) analysis.

2.2. Catalytic reactions

Under typical conditions, bromobenzene (0.2 mol; Tokyo Kasei Chemicals Ltd., Japan), phenylboronic acid (0.32 mol; Tokyo Kasei Chemicals Ltd., Japan), K_2CO_3 (0.4 mol; Wako Chemicals Ltd., Osaka, Japan), o-xylene (solvent, 560 mL, Wako Chemicals Ltd., Osaka, Japan), and 0.4 wt.% Pd/USY catalyst (0.5 mg, Pd: 1.9×10^{-8} mol), weighed using an electronic microbalance, were used for the Suzuki–Miyaura reactions. A 6% H_2/94% Ar flow at a rate of 30 mL min^{-1} was introduced into the reactant solution using a glass capillary tube before and during the reaction, for 1 h at r.t. A three-necked flask (1 L) was placed in an oil bath, preheated to the required temperature, and subjected to vigorous stirring. The reaction was performed at 383 K. Suzuki–Miyaura reactions using chlorobenzene derivatives were performed under similar conditions, except for the use of DMF + H_2O (1.5 vol.%) and Cs_2CO_3 as the solvent and base, respectively. The reactions were performed in an Ar atmosphere. After reaction, the reaction mixture was cooled to r.t., and the solution was analyzed using a Shimadzu 2010 Gas Chromatograph equipped with an InertCap 5 (30 m) capillary column

(Shimadzu Corp., Kyoto, Japan). Tridecane was used as the internal standard.

2.3. Pd K-edge and L_3-edge XAFS measurements and data analysis

Pd K-edge and Pd L_3-edge XAFS data were obtained from synchrotron radiation experiments performed at the BL01B1 station, with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2009B1107), and the BL10 station at the Ritsumeikan University SR Center, respectively. Pd K-edge XAFS data were collected in the quick mode; a Si(1 1 1) monochromator was continuously moved from 4.75° to 4.40° for 5 min. The beam size was 5 mm (horizontal) × 0.8 mm (vertical) at the sample position. For the Pd K-edge XAFS measurements, 6% H_2 was bubbled through a mixture of Pd/USY in o-xylene, and the treated Pd/USY was transferred to a plastic cell at r.t. without contact with air. The X-ray path length of the plastic cell was 2 cm. In the EXAFS analysis, oscillations were extracted by a spline smoothing method. The Fourier transformation of the k^3-weighted EXAFS oscillations and $k^3\chi(k)$ from the k space to the r space was carried out over the range 25–130 nm^{-1}. The inversely Fourier-filtered data were analyzed in the k range between 25 nm^{-1} and 130 nm^{-1} using a curve-fitting method. The inversely Fourier-filtered data were analyzed by the usual curve-fitting method, based on Eq. (1)

$$\chi^{(k)} = \sum N_j F_j(k) \exp(-2\sigma_j^2 k_j^2) \sin(2kr_j + \phi_j(k))/kr_j^2$$
$$k_j = (k^2 - 2m\Delta E_{0j}/\hbar^2)^{1/2}$$
(1)

where N_j, r_j, σ_j, and ΔE_{0j} represent the CN, the bond distance, the Debye–Waller factor, and the threshold energy difference between the reference and the sample, respectively. $F_j(k)$ and $\varphi_j(k)$ represent amplitude and phase shift functions, respectively. In the curve-fitting analysis, the empirical phase shift and the amplitude functions of Pd–O and Pd–Pd were extracted from the data obtained for PdO and Pd foils, respectively. CdS was used as the reference for Pd–Si/Al, as described in the literature [32].

For the collection of Pd L_3-edge XAFS data, the Pd/USY treated by bubbling 6% H_2 in o-xylene was transferred to a polyethylene bag (thickness = 10 μm) at r.t. Pd L_3-edge X-ray absorption near edge structure (XANES) data were recorded under He at atmospheric pressure in a fluorescence mode. A Ge(1 1 1) monochromator was moved stepwise from 37.3° to 35.0° for 30 min. The XAFS data were analyzed using the REX2000 (ver. 2.5) program developed by Rigaku Ltd., Tokyo, Japan. Error bars for each parameter in the EXAFS curve fitting were estimated by stepping each parameter, while optimizing the other parameter, with R factor becomes two times as its minimum value.

2.4. IRMS-TPD of NH_3

A Fourier-transform IR (FT-IR) spectrometer (Perkin-Elmer Spectrum-One; Perkin-Elmer, Waltham, MA, USA) and a mass spectrometer (Pfeiffer QME200; Pfeiffer, Asslar, Germany) were connected with a vacuum line kept at 3.3 kPa through which He was allowed to flow as the carrier (flow rate, 110 mL min^{-1}). An IR beam was transmitted to a self-compressed disk (5 mg and 10 mm in diameter). Details of the experimental apparatus have been described elsewhere [33]. After evacuation of the sample at 773 K, IR spectra were recorded before NH_3 adsorption at 10 K intervals from 373 to 773 K, while the temperature was increased at a rate of 10 K min^{-1} ($N(T)$, recorded). The bed temperature was then lowered to 373 K, at which point NH_3 was adsorbed at 13 kPa, and then gas-phase NH_3 was evacuated for 30 min. IR spectra were again measured at 10 K intervals from 373 to 773 K, while the temperature was raised ($A(T)$, recorded). The difference spectrum, i.e., $A(T) - N(T)$, was calculated at each temperature, and