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Construction of 2-(2′-Hydroxy-5′-methylphenyl)benzotriazole over Pd/γ-Al_2O_3 by a Continuous Process

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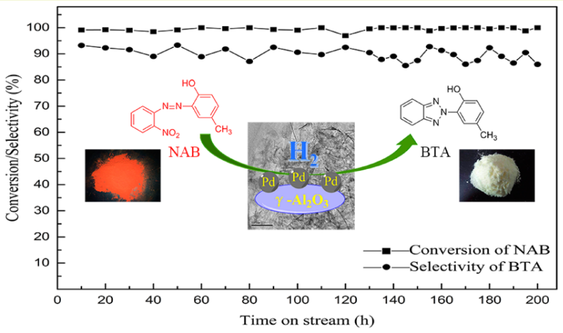
ABSTRACT: The synthesis of 2-(2′-hydroxy-5′-methylphenyl)-benzotriazole from 2-nitro-2′-hydroxy-5′-methylazobenzene over Pd/γ-Al_2O_3 in a fixed-bed reactor was investigated. Pd/γ-Al_2O_3 catalysts were prepared by two methods and characterized by XRD, TEM, H_2-TPR, and N_2 adsorption−desorption. Employed in the above reaction, the palladium catalyst impregnated in hydrochloric acid exhibited much better catalytic performance than that impregnated in ammonia−water, which was possibly attributed to the better dispersion of palladium crystals on γ-Al_2O_3. This result demonstrated that the preparation process of the catalyst was very important. Furthermore, the reaction parameters were optimized. Under the optimized conditions (toluene, NAB/triethylamine molar ratio 1:2, 60 °C, 2.5 MPa hydrogen pressure, 0.23 h^{-1} liquid hourly space velocity), about 90% yield of 2-(2′-hydroxy-5′-methylphenyl)benzotriazole was obtained. Finally, the time on stream performance of the catalyst was evaluated, and the reaction could proceed effectively over 200 h without deactivation of the catalyst.



KEYWORDS: *Benzotriazole, Catalytic hydrogenation, Palladium catalyst, Continuous synthesis, Solvent effect*

■ INTRODUCTION

2-(2′-Hydroxy-5′-methylphenyl)benzotriazole (BTA) is one of the most important ultraviolet absorbers and is widely employed for polymer materials,[1−3] so its synthesis attracts intensive attention. Normally, BTA is manufactured by the reductive cyclization of 2-nitro-2′-hydroxy-5′-methylazobenzene (NAB) in the presence of zinc dust/sodium hydroxide,[4−6] alkali sulfides,[7] thiourea S, S-dioxide/sodium hydroxide,[8] hydrazine hydrate/sodium hydroxide,[9] or SmI_2/THF.[10] Unfortunately, serious environmental contamination was always inevitable, which immensely inhibited the development of a BTA ultraviolet absorber. Thus, the construction of benzotriazole by catalytic hydrogenation is proposed as an alternative method with the consideration that only water is formed with the desired product during the reaction, which can fully solve the serious environmental pollution caused by the production of BTA. However, except for BTA, the construction of benzotriazole heterocycle by hydrogenation always yields *o*-phenylenediamine and 2-amino-p-cresol,[11] so it leads to poor BTA selectivity. Although few patents[12−14] reported the catalytic hydrogenation of NAB to BTA in satisfied yield, the only results were provided without any explanation. Worse yet, the above-mentioned synthetic methods of BTA were all carried out in a flask or autoclave. These contaminated operations and tedious workup procedures also hindered the development of BTA. So an efficient and green process is still required for the production of BTA.

In this paper, we tried to establish a green synthetic method for BTA by catalytic hydrogenation in a fixed-bed reactor. Copper, nickel, cobalt, and palladium supported on γ-Al_2O_3 were prepared and employed for the continuous synthesis of BTA from NAB, in which Pd/γ-Al_2O_3 (H) exhibited the best catalytic performance. Subsequently, these catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), H_2-temperature-programmed reduction (H_2-TPR), and nitrogen adsorption−desorption measurements to investigate the structure−activity relationship. Besides, reaction parameters, including solvent, base, palladium load, NAB/base molar ratio, temperature, hydrogen pressure, and liquid hourly space velocity (LHSV) were also optimized. Under the optimized condition, the time on stream performance of the catalyst was evaluated.

■ EXPERIMENTAL SECTION

Reagents. Palladium(II) chloride (98 wt %) was purchased from Tianjin Heowns Biochemical Technology Co., Ltd., Tianjin, China. 1,4-Dioxane (AR), *o*-xylene (AR), *p*-xylene (AR), toluene (AR), triethylamine (AR), *n*-butylamine (AR), and diethylamine (AR) were

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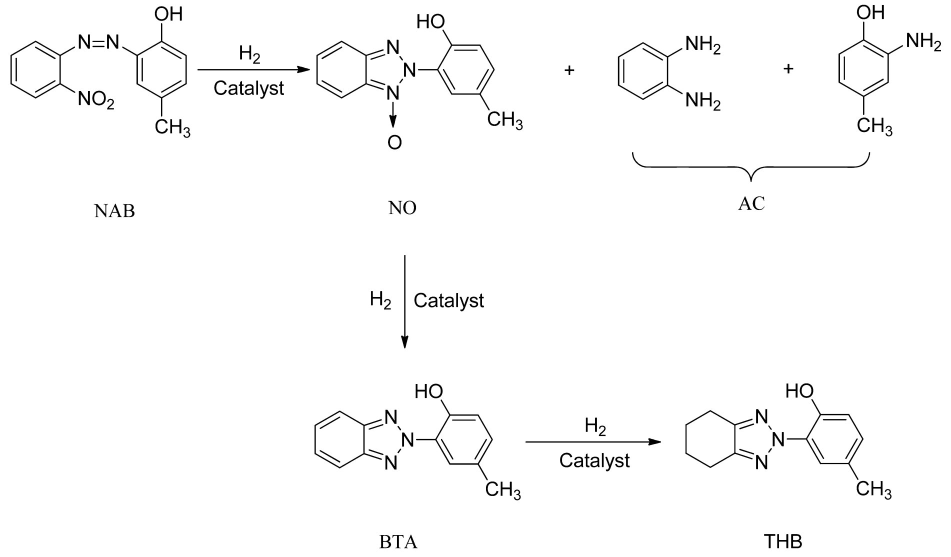
Scheme 1. Catalytic Hydrogenation of NAB



obtained from Tianjin Jiangtian Chemical Co., Ltd., Tianjin, China. Pseudo-boehmite was provided by Jiangyan Chemical Auxiliary Factory, Jiangyan, China. Commercially available reagents were used without further purification. 2-Nitro-2′-hydroxy-5′-methylazobenzene (≥90%, determined by HPLC) was prepared by the customary procedures of diazotization and coupling.[15]

Preparation of Catalysts. The Pd/γ-Al_2O_3 catalyst was prepared by incipient wetness impregnation, and the experimental details are described as follows: Initially, 50.00 g of pseudo-boehmite was kneaded vigorously with 60 mL water. The mixture was molded into a bar with a diameter of 3 mm by an extruder, dried at 120 °C for 6 h, and then calcined at 500 °C for another 4 h to yield supports. Furthermore, 0.26 g of palladium(II) chloride was respectively dissolved into 21 mL of ammonia–water and 8 wt % hydrochloric acid solution. The above-obtained supports (15.55 g) were respectively impregnated into these two solutions. After 12 h, the bars were successively dried in air at 120 °C for 6 h, calcined at 500 °C for 4 h, and then reduced at 300 °C in a hydrogen stream at a flow rate of 10 mL/min (1 MPa) for 3 h before use. These obtained catalysts were denoted as 1%Pd/γ-Al_2O_3 (N) and 1%Pd/γ-Al_2O_3 (H), respectively. In addition, other Pd/γ-Al_2O_3 catalysts with different palladium loads were also prepared and hereinafter referred as xPd/γ-Al_2O_3 (x = 0.25–3%).

Cu/γ-Al_2O_3, Ni/γ-Al_2O_3, and Co/γ-Al_2O_3 used in this study were prepared by the coprecipitation-kneading method.[16−18] For example, 20%Ni/γ-Al_2O_3 (content of Ni in the catalyst was 20 wt %) was prepared as follows: A solution of 50.89 g of $Ni(NO_3)_2 \cdot 6H_2O$ in 300 mL of water and a solution of 20.40 g of sodium carbonate in 300 mL of water were added simultaneously into 300 mL of water under mechanical stirring. The reaction mixture was aged for 1 h. The precipitate was filtered, washed with water, and dried in air at 120 °C for 6 h. The obtained solid was pulverized. The powder was kneaded with a mixture of 30.30 g of pseudo-boehmite and 50 mL of water and then molded to bars with a diameter of 3 mm. After being dried in air at 120 °C for 6 h, the bars were calcined at 500 °C for 4 h and reduced at 360 °C in a hydrogen stream at a flow rate of 10 mL/min (1 MPa) for 3 h before use.

Catalyst Characterization. The XRD patterns were collected on a Rigaku D/max 2500 (Rigaku Corporation, Japan) using a Cu Kα X-ray source (40 kV, 100 mA) in the range of 5−80°. Transmission electron microscope (TEM) micrographs were obtained with a Tecnai G2 F20 high resolution analytical electron microscope (FEI, The Netherlands) operating at an electron beam voltage of 200 kV. Powder samples were dispersed onto a carbon-coated copper grid for TEM/EDX analysis. H_2-temperature-programmed reduction (H_2-TPR) was measured using Thermo-Finnigan TPDRO 1100 with a temperature range from ambient temperature to 900 °C at a rate of 10 °C/min and a gas flow of 5% H_2 in nitrogen (20 mL/min). The specific surface areas were determined by the Brunauer−Emmer−Teller (BET) method with N_2 adsorption−desorption measurements at a liquid nitrogen temperature using a NOVA 2000e analyzer (Quantachrome, U.S.A.). The pore size distributions were obtained using the method of Barret−Joyner−Halenda (BJH). The actual weight percent of Pd in each catalyst was determined by an ICP-AES instrument.[19]

General Procedure for the Catalytic Hydrogenation of 2-Nitro-2′-hydroxy-5′-methylazobenzene. The catalytic hydrogenation of 2-nitro-2′-hydroxy-5′-methylazobenzene (NAB) to 2-(2′-hydroxy-5′-methylphenyl)benzotriazole (BTA) was carried out in a tubular, fixed-bed reactor with an inner diameter of 15 mm and a length of 650 mm, which was charged with 40 mL of catalysts under hydrogen atmosphere. A solution of NAB (5 wt %) and organic base in a suitable solvent was dosed into the reactor by a syringe pump. The temperature in the reaction zone was measured with a thermocouple placed in the center of the tube and regulated by use of a proportion integration differentiation (PID) cascade controller. The hydrogen pressure in the reaction system was set by use of a hydrogen regulator. The reaction mixture was analyzed by high performance liquid chromatography (HPLC) with a column of Extend C18 (250 mm × 4.6 mm, 10 μm, Angilent technologies, U.S.A.).

■ RESULTS AND DISCUSSION

Catalyst Selection. The catalytic hydrogenation of NAB is quite complicated because the azo and nitro groups coexist in the molecule. Thus, it is hard to control the hydrogenation pathway. In fact, besides BTA, a number of compounds, including 2-amino-p-cresol, *o*-phenylenediamine (AC, amino compounds),[11] 2-(2′-hydroxy-5′-methylphenyl)benzotriazole N-oxide (NO),[20,21] and tetrahydro-2-(2′-hydroxy-5′-methylphenyl)benzotriazole (THB),[22,23] were detected in this reaction mixture (Scheme 1). So the property of the catalyst is the key to improve the selectivity of BTA. First, 20%Cu/γ-Al_2O_3, 20%Ni/γ-Al_2O_3, and 20%Co/γ-Al_2O_3 were prepared and employed for this catalytic hydrogenation. The results are summarized in Table 1. No matter which catalyst was used, the conversion of NAB was satisfied (≥88.93%), but the selectivity of BTA was different from each other. The selectivity of BTA over 20%Cu/γ-Al_2O_3 was up to 44.84%, the best among these three catalysts. However, it was still at a low level. Subsequently, the catalytic hydrogenation of NAB to BTA was respectively carried out over 1%Pd/γ-Al_2O_3 (N) and 1%

Table 1. Catalytic Hydrogenation of NAB over Several Catalysts[a]

catalyst	conversion[b] (%)	selectivity[c] (%)
20%Cu/γ-Al_2O_3	88.93	44.84
20%Ni/γ-Al_2O_3	96.03	39.96
20%Co/γ-Al_2O_3	94.77	2.18
1%Pd/γ-Al_2O_3 (N)	100	17.34
1%Pd/γ-Al_2O_3 (H)	100	61.45

[a] Reaction conditions: solvent, 1,4-dioxane; base, triethylamine; molar ratio of NAB/triethylamine, 1:2; temperature, 110 °C; hydrogen pressure, 3.5 MPa; and LHSV, 0.45 h^{-1}. Each data point is an average of three or more runs. [b] Conversion of NAB. [c] Selectivity of BTA.

Pd/γ-Al_2O_3 (H) to improve the selectivity of BTA. Surprisingly, these two catalysts presented distinct catalytic performance. When 1%Pd/γ-Al_2O_3 (N) was used for this hydrogenation, the selectivity of BTA was only 17.34% despite 100% conversion of NAB. However, 61.45% selectivity of BTA was achieved with 1%Pd/γ-Al_2O_3 (H) as the catalyst. Obviously, catalyst preparation technology had a significant effect on their catalytic properties. Therefore, 1%Pd/γ-Al_2O_3 (N) and 1%Pd/γ-Al_2O_3 (H) were characterized by XRD, TEM, H_2-TPR, and N_2 adsorption−desorption measurements.

Catalyst Characterization. *XRD.* Figure 1 shows the XRD curves of 1%Pd/γ-Al_2O_3 (N), 1%Pd/γ-Al_2O_3 (H), and the support γ-Al_2O_3. All samples presented a clear γ-Al_2O_3 structure as reflected in the X-ray diffraction peaks at 2θ = 66.7°, 45.8°, and 37.6°. Except for γ-Al_2O_3, profiles of the two catalysts showed a diffraction peak (2θ = 39.8°) associated with the metal palladium (111) phase.[24] The presence of γ-Al_2O_3 and palladium diffraction peaks confirmed that palladium was successfully supported on γ-Al_2O_3. Furthermore, the metal palladium diffraction peak of 1%Pd/γ-Al_2O_3 (N) was more intense than that of 1%Pd/γ-Al_2O_3 (H), indicating that the dispersion of palladium particles could be influenced by the catalyst preparation method.[25] The dispersion of palladium species on 1%Pd/γ-Al_2O_3 (H) was better than that on 1%Pd/γ-Al_2O_3 (N), resulting in 1%Pd/γ-Al_2O_3 (H) exhibiting better catalytic performance.

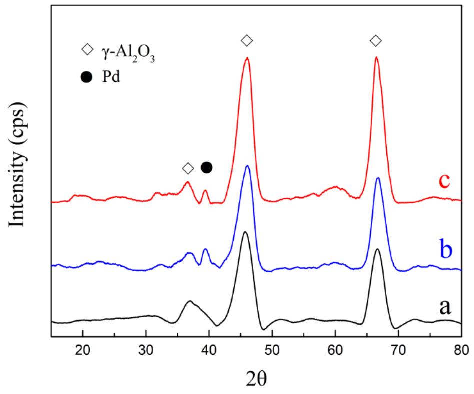


Figure 1. XRD patterns for (a) γ-Al_2O_3, (b) 1%Pd/γ-Al_2O_3 (N), and (c) 1%Pd/γ-Al_2O_3 (H).

TEM. The morphology and size of the palladium particles on 1%Pd/γ-Al_2O_3 (N) and 1%Pd/γ-Al_2O_3 (H) were studied by TEM and are described in Figure 2. It was obvious that palladium particles were uniformly dispersed on the surface of 1%Pd/γ-Al_2O_3 (H), and its size was smaller than that of 1%Pd/γ-Al_2O_3 (N). This demonstrated that the dispersion of palladium on 1%Pd/γ-Al_2O_3 (H) was much better than that on 1%Pd/γ-Al_2O_3 (N). Zhu et al. reported that palladium precursors displayed an important influence on the crystallite size and the dispersion of the palladium active phase.[25] As is well known, H_2PdCl_4 is normally obtained from hydrochloric acid and $PdCl_2$, while $Pd(NH_3)_4Cl_2$ is obtained from ammonia−water and $PdCl_2$, so the two different precursors presumably affect the dispersion of palladium on the support. Moreover, EDX analyses detected the presence of palladium, which meant that the two catalysts were successfully synthesized. The above analyses agreed well with the XRD results.

H_2-TPR. H_2-temperature-programmed reduction (H_2-TPR) measurements were carried out to investigate the reduction patterns of palladium species on 1%Pd/γ-Al_2O_3 (N) and 1% Pd/γ-Al_2O_3 (H). As shown in Figure 3, there were two reduction peaks at 70−175 °C and 175−300 °C, denoted as α and β, respectively. The α peak could be attributed to the reduction of PdO to metallic palladium, while the β peak was assigned to the reduction of the species formed between PdO and γ-Al_2O_3.[25−27] Compared with 1%Pd/γ-Al_2O_3 (N), the β peak of 1%Pd/γ-Al_2O_3 (H) dropped about 20 °C. The decrease in reduction temperature meant that there existed better dispersion of the palladium precursor on the surface of 1%Pd/γ-Al_2O_3 (H), which was in accordance with the results of XRD and TEM characterizations.

Physical and Textural Properties. The nitrogen adsorption−desorption isotherms of γ-Al_2O_3, 1%Pd/γ-Al_2O_3 (N), and 1%Pd/γ-Al_2O_3 (H) at 77 K are depicted in Figure 4. All of them displayed a typical isotherm of mesoporous materials with a hysteresis loop. Compared with γ-Al_2O_3 and 1%Pd/γ-Al_2O_3 (N), the hysteresis loop of 1%Pd/γ-Al_2O_3 (H) obviously diminished. Thus, the BET surface area and the pore structure of 1%Pd/γ-Al_2O_3 (H) should be remarkably different from γ-Al_2O_3 and 1%Pd/γ-Al_2O_3 (N). Meanwhile, the pore size distribution curves indicated that the pore size of 1%Pd/γ-Al_2O_3 (H) was the smallest among these three samples. Besides, the BET specific surface, the total pore volume and average pore radius of γ-Al_2O_3, 1%Pd/γ-Al_2O_3 (N), and 1%Pd/γ-Al_2O_3 (H) are summarized in Table 2. It was somewhat surprising that the BET specific surface and total pore volume of 1%Pd/γ-Al_2O_3 (H) were 1130 m^2/g and 1.87 cm^3/g, respectively, which were much larger than the other two samples, and it would result in better dispersion of palladium. Therefore, 1%Pd/γ-Al_2O_3 (H) exhibited the best catalytic performance in the catalytic hydrogenation of NAB to BTA. The results were consistent with XRD, TEM, and H_2-TPR characterizations.

In order to understand the increase in the BET surface area and pore volume of 1%Pd/γ-Al_2O_3 (H) more clearly, the support was respectively treated by 8 wt % hydrochloric acid solution and ammonia−water under the same conditions as the catalyst preparation, denoted as γ-Al_2O_3 (H) and γ-Al_2O_3 (N), and then characterized by a nitrogen adsorption−desorption experiment. As shown in Table 2, the result revealed that the BET surface area and pore volume of γ-Al_2O_3 treated by acid increased to 1219 m^2/g and 1.68 cm^3/g, respectively. Simultaneously, the average pore radius of γ-Al_2O_3 (H) became much smaller than γ-Al_2O_3. However, there was no significant difference between γ-Al_2O_3 (N) and γ-Al_2O_3. It was obvious that acid-impregnation of γ-Al_2O_3 indeed resulted in the sharp increase in BET surface area and pore volume, as well as the

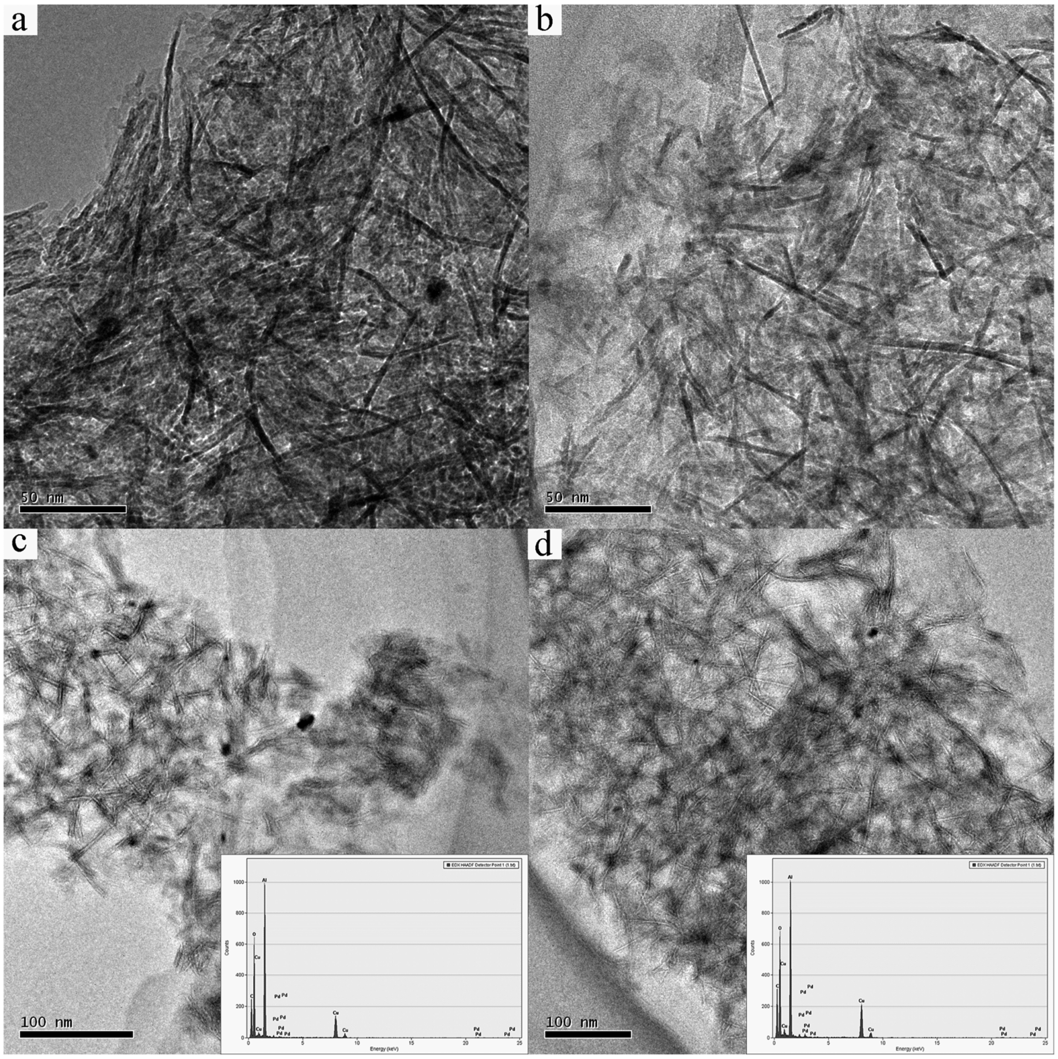


Figure 2. TEM images and EDX spectra of (a, c) 1%Pd/γ-Al_2O_3 (N) and (b, d) 1%Pd/γ-Al_2O_3 (H).

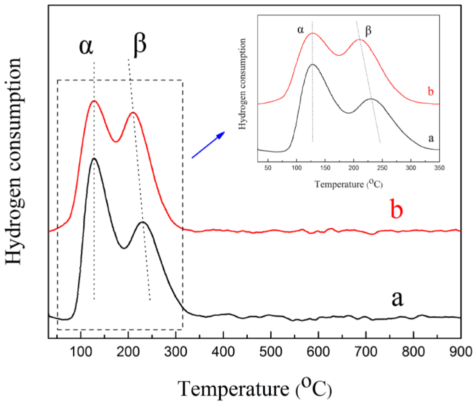


Figure 3. H_2-TPR curves of precursors of (a) 1%Pd/γ-Al_2O_3 (N) and (b) 1%Pd/γ-Al_2O_3 (H).

remarkable decrease in the pore radius of γ-Al_2O_3, which was also consistent with the obvious difference between the nitrogen adsorption−desorption isotherms of 1%Pd/γ-Al_2O_3 (H) and γ-Al_2O_3. Some reports[28,29] claimed that acid treatment in the preparing process results in the increase in BET surface area and decrease in pore radius of Al_2O_3, without detailed and convincing explanations. We presumably propose that, in the preparing process, the corrosion of the support by hydrochloric acid may cause a change in the catalyst pore structure, which is the reason for the aforementioned results.

Effect of Solvent. Table 3 reveals the influence of solvent on the catalytic hydrogenation of NAB to BTA. Because of the poor solubility of NAB, only 1,4-dioxane, *o*-xylene, *p*-xylene, and toluene were employed in this reaction. It was found that the selectivity of BTA was obviously affected by solvent polarity. Nonpolar or weak polar solvents, such as *o*-xylene, *p*-xylene, and toluene, yielded better selectivity of BTA (≥84.60) than 1,4-dioxane (73.28%). The maximum selectivity of BTA (88.11%) was achieved with toluene as solvent. As is well known, the solvent normally displays a significant effect on the process of catalytic hydrogenation, such as the solubility of hydrogen, solvation of reactants and products, and adsorption and desorption of solvents, reactants, and products, etc.[30] Although the solvent effect on the selectivity over metal-supported catalysts is difficult to explain,[31] a speculation can be made that the π−π stacking interaction between toluene and BTA might be the key factor in the increase in BTA selectivity. This interaction would enhance BTA desorption from the catalyst surface, which correspondingly inhibited the formation of AC and THB. In addition, as shown in Table 3, the kind of base (primary amine, secondary amine, or tertiary amine) had

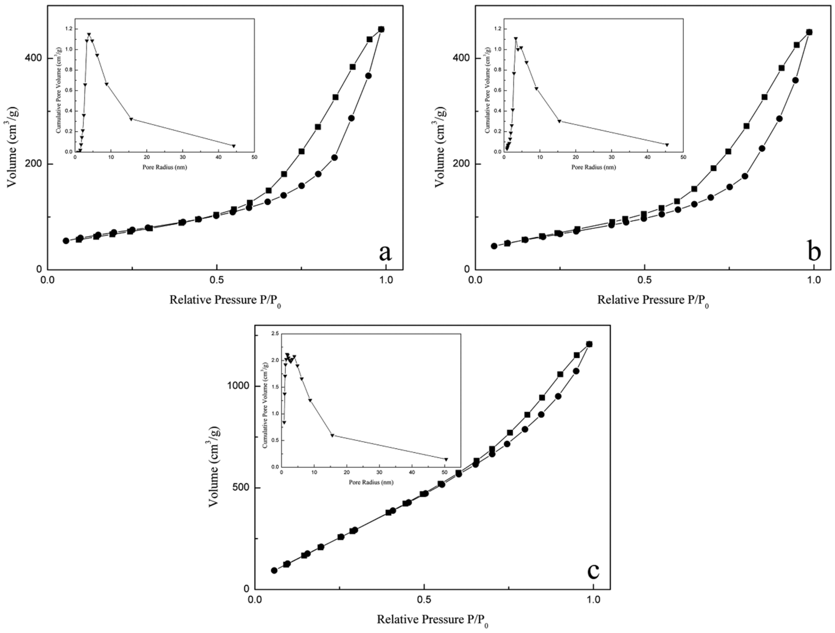


Figure 4. N_2 adsorption and desorption isotherms and pore distributions of (a) γ-Al_2O_3, (b) 1%Pd/γ-Al_2O_3 (N), and (c) 1%Pd/γ-Al_2O_3 (H).

Table 2. Physical and Textural Properties of γ-Al_2O_3, γ-Al_2O_3 (N), γ-Al_2O_3 (H), 1%Pd/γ-Al_2O_3 (N), and 1%Pd/γ-Al_2O_3 (H)

sample	Pd (wt %)[a]	S_{BET} (m^2/g)	V_{total} (cm^3/g)	$R_{average}$ (nm)
γ-Al_2O_3	–	252	0.70	5.59
γ-Al_2O_3 (N)	–	250	0.69	5.51
γ-Al_2O_3 (H)	–	1219	1.68	2.76
1%Pd/γ-Al_2O_3 (N)	0.72	232	0.70	6.01
1%Pd/γ-Al_2O_3 (H)	0.70	1130	1.87	3.30

[a] wt % of palladium is measured by ICP-AES.

no significant effect on the catalytic hydrogenation of NAB to BTA.

Reaction Parameters. Considering the complexity of the catalytic hydrogenation of NAB, the optimization of reaction conditions is also important for the construction of benzotriazoles. Therefore, with Pd/γ-Al_2O_3 (H) as the catalyst, the influence of palladium load, NAB/base molar ratio, temperature, hydrogen pressure, and LHSV on this reaction were investigated.

Initially, the effect of palladium load on the catalytic hydrogenation of NAB was investigated, and the results are described in Table 4. It was found that 1%Pd/γ-Al_2O_3 (H) displayed the desired behavior for the catalytic hydrogenation of NAB.

The influence of NAB/triethylamine molar ratio on this reaction was investigated, and the results are shown in Figure 5a. It is shown that with a decrease in NAB/triethylamine molar ratio from 1:1 to 1:2, the selectivity of BTA remarkably increased and then remained basically unchanged. As the molar ratio of NAB and triethylamine further decreased to 1:4, the selectivity of BTA decreased obviously. The increase in triethylamine concentration would lead to the decrease in NAB solubility in toluene. This might be the main reason for the decrease in BTA selectivity. Thus, 1:2 was used for the following study.

The catalytic hydrogenation of NAB over Pd/γ-Al_2O_3 (H) was examined at a temperature range from 50 to 80 °C. It was clear from the data in Figure 5b that 60−70 °C might be the optimal reaction temperature. Hydrogen pressure had a significant influence on the catalytic hydrogenation of NAB to BTA. As shown in Figure 5c, the selectivity of BTA was maximum (93.41%) under 2.5 MPa hydrogen pressure.

Liquid hourly space velocity (LHSV) is another important parameter for catalytic hydrogenation of NAB in a fixed-bed reactor. So the catalytic performance of 1%Pd/Al_2O_3 (H)

Table 3. Effects of Solvent and Base on Catalytic Hydrogenation of NAB[a]

			selectivity (%)				
solvent	base	conversion[b] (%)	AC	NO	BTA	THB	others[c]
1,4-dioxane	triethylamine	99.65	15.15	3.83	73.28	1.15	6.24
o-xylene	triethylamine	99.07	3.23	5.49	85.33	–	5.02
p-xylene	triethylamine	100	3.55	3.41	84.60	–	8.44
toluene	triethylamine	99.12	1.56	3.95	88.11	–	5.50
toluene	diethylamine	98.74	2.41	5.32	85.68	–	5.33
toluene	*n*-butylamine	98.41	3.20	–	90.46	–	4.75

[a] Reaction conditions: catalyst, 1%Pd/γ-Al_2O_3 (H); molar ratio of NAB/base, 1:2; temperature, 60 °C; hydrogen pressure, 3.5 MPa; and LHSV, 0.15 h^{-1}. Each data point is an average of three or more runs. [b] Conversion of NAB. [c] Including contaminations in raw material, errors of measurement instrument and trace impurities produced in the reaction.

Table 4. Effect of Palladium Load on the Catalytic Hydrogenation of NAB[a]

catalyst	conversion[b] (%)	selectivity (%) AC	NO	BTA	THB	others[c]
0.25%Pd/γ-Al_2O_3 (H)	99.60	8.90	15.97	66.47	–	8.26
0.5%Pd/γ-Al_2O_3 (H)	99.61	8.13	11.61	70.91	1.02	7.94
1%Pd/γ-Al_2O_3 (H)	99.65	15.15	3.83	73.28	1.15	6.24
1.5%Pd/γ-Al_2O_3 (H)	99.67	15.35	3.78	59.83	13.07	7.64
3%Pd/γ-Al_2O_3 (H)	100	17.26	3.18	–	71.77	7.79

[a] Reaction conditions: solvent, 1,4-dioxane; base, triethylamine; molar ratio of NAB/triethylamine, 1:2; temperature, 60 °C; hydrogen pressure, 3.5 MPa; and LHSV, 0.15 h^{-1}. Each data point is an average of three or more runs. [b] Conversion of NAB. [c] Including contaminations in raw material, errors of measurement instrument and trace impurities produced in the reaction.

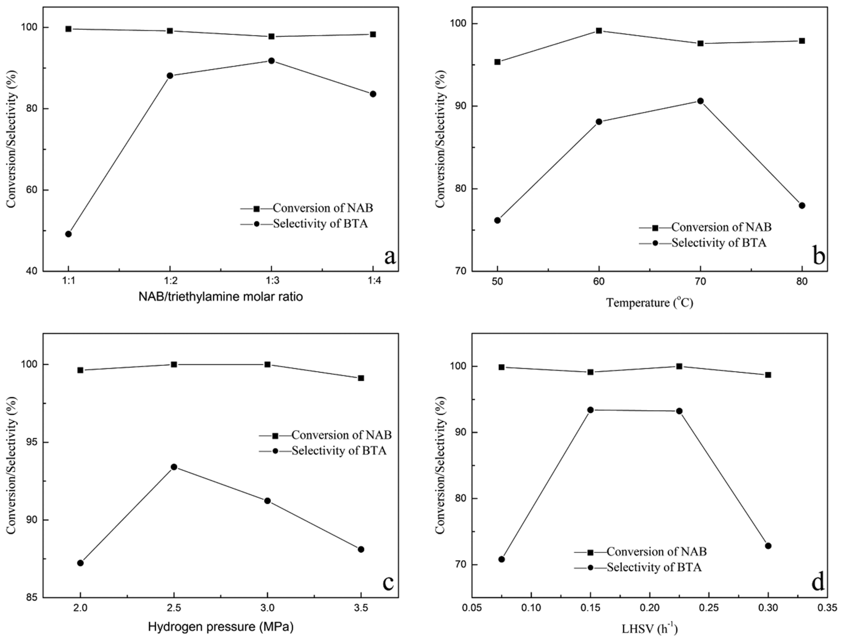


Figure 5. (a) Influence of NAB/triethylamine molar ratio on the conversion of NAB and the selectivity of BTA: catalyst, 1%Pd/γ-Al_2O_3 (H); temperature, 60 °C; hydrogen pressure, 3.5 MPa; and LHSV, 0.15 h^{-1}. (b) Influence of reaction temperature on the conversion of NAB and the selectivity of BTA: catalyst, 1%Pd/γ-Al_2O_3 (H); molar ratio of NAB/triethylamine, 1:2; hydrogen pressure, 3.5 MPa; and LHSV, 0.15 h^{-1}. (c) Influence of hydrogen pressure on the conversion of NAB and the selectivity of BTA: catalyst, 1%Pd/γ-Al_2O_3 (H); molar ratio of NAB/triethylamine, 1:2; temperature, 60 °C; and LHSV, 0.15 h^{-1}. (d) Influence of LHSV on the conversion of NAB and the selectivity of BTA: catalyst, 1%Pd/γ-Al_2O_3 (H); molar ratio of NAB/triethylamine, 1:2; temperature, 60 °C; and hydrogen pressure, 2.5 MPa. Each data point is an average of three or more runs.

under different LHSV was evaluated (Figure 5d). When the LHSV was 0.15–0.23 h^{-1}, the selectivity of BTA reached the maximum. Taking productivity into consideration, 0.23 h^{-1} was chosen as the optimum LHSV.

Stability of 1%Pd/Al_2O_3 (H). The stability test of 1%Pd/γ-Al_2O_3 (H) was performed under the optimum conditions (solvent, toluene; NAB/triethylamine molar ratio, 1:2; temperature, 60 °C; hydrogen pressure, 2.5 MPa; and LHSV, 0.23 h^{-1}) in the fixed-bed reactor, and the results are shown in Figure 6. It was found that no notable deactivation of this catalyst in activity or BTA selectivity was observed in 200 h, and the yield of BTA remained above 85%, which indicated that 1%Pd/γ-Al_2O_3 (H) exhibited excellent stability.

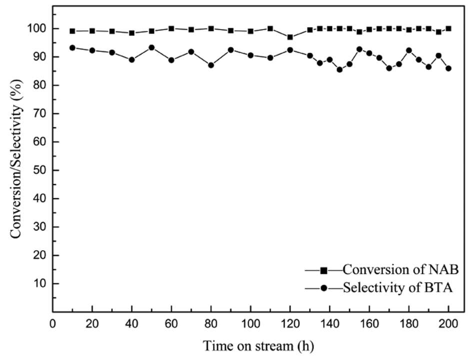


Figure 6. Time on stream performance of 1%Pd/Al_2O_3 (H).

■ CONCLUSION

The synthesis of BTA from NAB over Pd/γ-Al_2O_3 was investigated, and a green continuous synthetic technology of BTA was successfully established. Palladium catalysts were prepared by two preparation methods and characterized by XRD, TEM, H_2-TPR, and N_2 adsorption–desorption. The results revealed that using hydrochloric acid as the impregnation solution could enhance the dispersion of Pd crystals, and 1%Pd/γ-Al_2O_3 (H) exhibited better catalytic performance than 1%Pd/γ-Al_2O_3 (N). It was probably due to the difference of palladium precursors and the support modified by hydrochloric acid. This result demonstrated that the preparation process of the catalyst was very important. Meanwhile, the reaction parameters were optimized. Finally, the stability test of 1%Pd/γ-Al_2O_3 (H) was performed under the optimized conditions (solvent, toluene; NAB/triethylamine molar ratio; 1:2; temperature, 60 °C; hydrogen pressure, 2.5 MPa; and LHSV, 0.23 h^{-1}). The results showed that the catalyst could run over 200 h without obvious deactivation.

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Notes

The authors declare no competing financial interest.

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