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Efficient decarbonylation of 5-hydroxymethylfurfural over an Pd/Al_2O_3 catalyst: Preparation via electrostatic attraction between Pd(II) complex and anionic Al_2O_3

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ABSTRACT

Decarbonylation of 5-hydroxymethylfurfural (HMF) provides a potential way to utilize the abundant natural hexoses derived from cellulose or hemicellulose. Herein, we propose for the first time that a Pd/Al_2O_3 prepared based on an electrostatic attraction strategy can efficiently convert HMF into furfuryl alcohol (FOL). Ammonia solution with high pH value could realize the electrostatic attraction assumption in the interface of support and palladium complex, while diluted hydrochloric acid with low pH value could cause the instability of H^+ ions on Al_2O_3 surface, leading to larger Pd nanoparticles (NPs) of the catalyst and lowering the decarbonylation activity. A structure-sensitive behavior was discussed that the intrinsic activity of catalyst rised with the decreased size of Pd NPs, which could be illustrated by that the smaller particles exposed more defective Pd sites, on which the decarbonylation adsorption mode of $\eta^2(C, O)$ was preferred. FOL yield of 95% was obtained through modulation of reaction conditions.

1. Introduction

Noble catalysts, as widely known are expensive. How to improve the dispersion or to lower the loading of noble metal is the continued pursuit in catalysis research. Pd/Al_2O_3, as a commercially available catalyst, [1] has been widely used in the catalytic transformation, including hydrogenation [2–8] and hydrogenolysis [9] reactions, oxidation [10–13] and reduction [14–16] reactions, reforming [17] and isomerization [18] reactions, etc. The strong metal-support interaction and the synergistic effect of the metallic sites and the Lewis acid sites promise Pd/Al_2O_3 a good stability and superior catalytic performances. [17–19] Thus, preparing efficient Pd/Al_2O_3 catalyst is highly desirable but challenging. Generally, metallic nanoparticles (NPs) with small sizes exhibit high catalytic activity. [20–26] For example, anchoring Pd species onto the support through bifunctional ligands has been adopted to prepare highly dispersed Pd based catalysts. [27–29] However, the generally complicated preparation methods, such as vapor deposition, alcohol reduction or photodeposition method, restricted their application on a large scale. Incipient wetness impregnation is the most commonly used method to prepare supported noble metal catalysts, considering its safety, simpleness and low cost. [7,24,30–34] Therefore, it is of great significance to develop an effective impregnation method to promote dispersion of Pd/Al_2O_3 catalyst with small Pd NPs. Moreover, it would shed light on the preparation method of other noble metal catalysts.

The impregnation process usually involves different adsorption interactions between active species and the support, which could be tuned by properly choosing the metal compound, the carrier or the pH of the solution. [35,36] The adsorption of palladium complexes on alumina may results from either electrostatic interaction or from simple physisorption. The adsorption strength is affected by the pH of the impregnation solution, as either the charges of the complex or the electric state of the support surface is pH dependent. Al_2O_3 obtains large amount of hydroxyl groups on the surface especially in the presence of water. [37] In contact with the active phase solution, the surface —OH may undergo protonation (when the pH is below the isoelectric point (IEP) of the alumina) or deprotonation (when the pH > IEP of the support). [38] Thus, the support surface would be positively or negatively charged as shown in Scheme 1. Furthermore, the palladium complex could also be neg-

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$$Al-OH + H_3O^+ \rightleftharpoons Al-OH_2^+ + H_2O \qquad pH < IEP$$

$$Al-OH + OH^- \rightleftharpoons Al-O^- + H_2O \qquad pH > IEP$$

Scheme 1. Changes of surface charges on Al_2O_3 in solution at different pH values.

atively charged (for example in form of $[PdCl_4]^{2-}$ or $[PdCl_3]^-$ with high hydrochloric acid content) or positively charged (for example $[Pd(NH_3)_4]^{2+}$ with ammonia water) depending on the pH of solution. [39] On the basis of this understanding, it is envisaged that a highly dispersed Pd/Al_2O_3 could be prepared through electrostatic attraction between surface-charged support and metallic ions at low pH or at high pH. However, usually Pd/Al_2O_3 catalysts are prepared by acidic impregnation solution of palladium salts and are restricted to poor dispersion. [40–42] It even has been reported that a highly dispersed Pd/Al_2O_3 catalyst with high activity was prepared at pH = 10, while that prepared at pH = 4 was poorly dispersed. [43] This is not consistent with the electrostatic attraction mechanism so well and no work has illustrated this contradiction. Furthermore, though the adsorption isotherm of Pd (II) on alumina at different pH has been studied long ago [44], the effect of pH on the dispersion of catalysts and further on their performances has not been investigated systematically. In this work, we envisage promoting dispersion of Pd/Al_2O_3 via metal-support electrostatic attraction by tuning the pH of impregnation solution and further shed light on the action mechanism of the pH.

Recently, decarbonylation of 5-hydroxymethylfurfural (HMF, one of the key platform chemical in the biomass utilization from cellulose) [45] to furfuryl alcohol (FOL) has attracted much attention (Scheme 2) [46]. Presently, homogeneous (Ir compounds) [47] and heterogeneous catalyst (Pd/SBA-15) [46] have been investigated on decarbonylation of HMF aiming at a high FOL yield. However, the homogenous catalyst is unrecoverable and the heterogeneous Pd/SBA-15 is necessarily in need of molecule sieves for unclear reasons presently. Pd/Al_2O_3 has been used for decarbonylation of HMF, but the catalytic activity is remained to be promoted. [30] Furthermore, it has been reported that, decarbonylation of another platform chemical-furfural is highly structure sensitive, exhibiting high decarbonylation activity on small metallic particles. [25] Therefore, it is expected to be favorable to perform HMF decarbonylation on Pd/Al_2O_3 catalyst with smaller Pd NPs.

In this work, a wide scale of pH values (1–14) were investigated for preparation of Pd/Al_2O_3 catalyst. The surface charges of Al_2O_3 support and Pd complex are significantly pH-dependent, leading to different kind of interactions in the interface and resulting in various particle sizes. Decarbonylation performances were significantly improved by promoting dispersion of catalysts prepared in basic ammonia solution. The behavior of structure sensitivity exhibited by the catalytic performances, which are greatly influenced by metallic particle size is an important issue in heterogeneous catalysis. [48–50] Thus, the surface properties of catalysts were explored and their relationship with the size-sensitive behavior was discussed.

2. Experimental section

2.1. Preparation of catalysts

Typically, 0.42 g palladium chloride (Sigma-Aldrich) was dissolved in the mixture of 2 g 25% ammonia solution (Sinopharm Chemical Reagents) and 48 g deionized water. Then 15 g deionized water was added. The pH of this impregnation solution was 12. Then hydrochloric acid (Sinopharm Chemical Reagents) was used to modify the pH of the solution to 8 and 6 respectively. Pd/Al_2O_3 was prepared by impregnating 50 g Al_2O_3 (Aluminum Co., Ltd, of China) particles with 20–40 mesh in the different impregnation solutions for 5 h and drying at 80 °C for 12 h. The catalysts prepared by solution with pH = 12, 8, 6 are donated as PA-2, PA-3, PA-4. PA-1 was prepared in the impregnation solution that $PdCl_2$ dissolved in ammonia solution with the pH = 14. PA-5 was prepared in the impregnation solution that $PdCl_2$ dissolved in hydrochloric acid solution with pH = 1. All the Pd precursor solutions were put overnight and no precipitate was discovered. The calcined catalysts at 400 °C for 2 h in air are denoted as PA-X-C (X = 1, 2, 3, 4, 5). The Pd loading of all the catalysts is 0.5 wt%.

2.2. Activity tests

The catalytic tests were performed in a 50 mL stainless steel autoclave. Prior to the tests, the catalysts were reduced offline in H_2 flow at 200 °C for 2 h. In a typical run, 1 g HMF (Shanghai DEMO Medical Tech. Co., Ltd, China), 20 g 1, 4-dioxane (Sinopharm Chemical Reagents) and 0.20 g catalysts were introduced into the autoclave. Then, the reactor was purged with H_2 for five times to replace the air in the autoclave, and then was heated to 180 °C, stirred at 500 rpm. Thus, the reactions were conducted under the autogenous pressure. After the reaction, the autoclave was cooled down by ice-water bath. The gas was collected and analyzed offline by two gas chromatographs (GC) (models 6890N, Agilent, USA) equipped with a FID and a TCD detector respectively. The products in the liquid phase were separated from the catalyst by filtration and were analyzed by a GC (model 6890N, Agilent; column: DB-WAXETR, 30 m*0.32 mm*0.5 um) equipped with a FID detector. The products in the gaseous phase were neglected with a content of less than 1% as determined by the gaseous analysis. The conversion and the selectivity were determined based on the area normalization method. The contents of FOL and HMF were also tested by an internal standard, which were consistent with the results of area normalization method.

2.3. Catalyst characterization

Zeta potential measurements were carried out on a Zeta Potential analyser (Malvern Nano-ZS-90) to determine the IEP of Al_2O_3. The Al_2O_3 powder was suspended in deionized water through ultrasonic vibration with a concentration of 1 mg/ml. Prior to the measurement, the pH value of the suspension was adjusted using 1 M HCl or 1 M NaOH solution.

The BET surface area (S_{BET}), pore size (D_p) and pore volume (V_P) were determined by N_2 physisorption at −196 °C at a micromeritics ASAP 2420 instrument. The samples were degassed under vacuum at 90 °C for 1 h and 300 °C for 8 h prior to the measurements.

Palladium dispersion was measured by CO chemisorption on Auto Chem. II 2920 equipment (Micromeritics, USA) at 50 °C with a pulse of 5% CO/95% He. Prior to the measurements, the samples were in situ reduced by flowing H_2 at 200 °C for 2 h and purged by flowing He at 250 °C for 30 min to remove the adsorbed hydrogen. The Pd dispersion was calculated based on an adsorption stoichiometry of one CO per exposed palladium atom.

X-ray photoelectron spectroscopy was measured on a Thermo XPS ESCALAB 250Xi spectrometer with a monochro-matic Alα (1486.8 eV) source. The XPS of reduced catalysts was recorded after in situ reduction by H_2 at 200 °C for 2 h, while that of calcined catalysts was scanned as received. The binding energies were calibrated with the reference of C1 s at 284.6 eV.

The ^{27}Al MAS NMR experiments of the dried catalysts were conducted on a Bruker Avance III 600 MHz Wide Bore spectrometer (14.2T), with the MAS spining rate at ~13 k Hz. The chemical shift is referenced to $Al(NO_3)_3$ solution at 0 ppm.