Understanding the underlying mechanism of improved selectivity in pd1 single-atom catalyzed hydrogenation reaction

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ARTICLE INFO

ABSTRACT

Supported metal single-atom catalysts (SACs) with maximized metal atom efficiency and unique catalytic properties have drawn tremendous attention in the catalysis field. In this work, we reported that in selective hydrogenation of 1,3-butadiene, graphene supported Pd_1 single atoms, synthesized by atomic layer deposition, exhibited expressively 100% butenes selectivity at 100% conversion at near ambient temperature, regardless of hydrogen partial pressures. The hydrogen reaction order was found to be about 1.2, indicating that hydrogenation dissociation is the rate-determining step. Combining with other structural characterization techniques, in situ X-ray absorption fine structure spectroscopy suggests that the Pd_1 single atom likely bonds to the graphene support through three Pd—C and one Pd—O—C coordinations. Density functional theory calculations show that 1,3-butadiene adsorbs on Pd_1 via a mono-π adsorption mode (-0.98 eV), much stronger than that of H_2 (-0.30 eV), which makes Pd_1 to be predominantly covered with a 1,3-butadiene molecule during reaction, consistent very well with the results of H-D exchange reaction. Facilitated by the bridging O atom in the Pd—O—C coordination, H_2 dissociates at the 1,3-butadiene covered Pd_1 atom in the heterolytic way, then hydrogenates the adsorbed 1,3-butadiene molecule by following the pseudo Horiuti-Polanyi mechanism. Distinct from its adsorption on extended Pd surfaces, such mono-π adsorption of 1,3-butadiene on Pd_1 favors 1-butene formation, but impedes the secondary hydrogenation to butane owing to intensified steric hindrance, thus yielding the expressively high butenes selectivity over Pd_1 SAC. These findings pave a new way to rational design SACs catalyst in selective hydrogenation reactions.

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1. Introduction

Supported metal catalysts are widely used in many industrial catalytic processes. Their catalytic performances are tightly related with the size and composition of metal nanoparticles (NPs). Reducing metal particle size to atomically dispersed metal single atoms, so-called single-atom catalysts (SACs), would maximize the metal utilization. Given their distinct geometric structures and discrete energy band structures from the counterpart of metal nanocrystals, atomically-dispersed metal atoms would modulate the adsorption of reactants considerably and change chemical bond breaking and making in catalysis, thus exhibiting very unique catalytic performance. As a consequence, SACs have drawn a rapid increase of attention in the catalysis field, since Zhang et al. reported that Pt_1/FeO_x SAC had high activity for both CO oxidation and preferential oxidation of CO in H_2 [1]. On the other hand, SACs bridge heterogeneous and homogeneous catalysis and have much simple active site structures. This is particularly useful for theoretical calculations by considering both the metal active site and the support without oversimplifying the catalyst structure, thereby greatly facilitating atomic-level insight of structure-activity relations [1–12].

Selective hydrogenation is an important catalytic process for chemical refining. The key issues are the low selectivity to the

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desired products at high conversions and catalyst deactivation caused by heavy coke formation [13]. Single-atom alloys (SAAs) and metal SACs have drawn particular interest in hydrogenation reactions. For examples, Sykes and co-workers reported that PdCu and PtCu SAAs had significantly higher selectivity in selective hydrogenation of acetylene and 1,3-butadiene than Pd NP catalyst [3,14]. Later they further demonstrated that coking formation could be remarkably inhibited on PtCu SAAs in the reaction of butane–deuterium isotope scrambling [15]. For SAC system, Zheng and co-workers reported that ethylene glycolate stabilized Pd_1 single atoms on TiO_2 exhibited very high catalytic activity in hydrogenation of C=C bonds and aldehydes, exceeding commercial Pd NP catalysts by a factor of 9 and 55, respectively [12]. López et al. reported that Pd_1 single atoms on graphitic carbon nitride showed high activity and high selectivity in hydrogenation of alkynes and nitrobenzenes [9]. Xu et al. showed that isolated Au^{3+} ions on a zirconia support was more active than Au NPs in selective hydrogenation of 1,3 butadiene to butenes, along with 100% butenes selectivity at a conversion of 90% at 120 °C [16]. Recently, we demonstrated that graphene supported Pd_1 single atoms fabricated by atomic layer deposition (ALD) showed extraordinarily high catalytic performance in selective hydrogenation of 1,3-butadiene, by yielding 100% butenes selectivity at a near complete conversion at 50 °C; in particular, the 1-butene selectivity was as high as 71%, the highest one in literature [10]. Therein isolated phenolic groups were found to be crucial for anchoring Pd_1 single atoms during ALD synthesis. Ex situ X-ray absorption fine structure spectroscopy (XAFS) suggested that the Pd_1 single atom bonds to one surface carbon atom, and one molecular oxygen along with one bridging oxygen between the Pd_1 atom and graphene support (this sample is denoted as Pd_1-O/graphene to empathize the bridging O atom).

In this work, in situ XAFS, H_2-temperature-programmed reduction (H_2-TPR), H-D exchange reaction, and density functional theory (DFT) calculations were further carried out to achieve atomic-level insight of detailed reaction mechanism as well as the critical role of the bridging oxygen atom in Pd_1-O/graphene catalyzed selective hydrogenation of 1,3-butadiene. In selective hydrogenation of 1,3-butadiene, we showed that variation of hydrogen partial pressures had essentially no impact on the butenes selectivity over Pd_1-O/graphene which preserved at 100% at compete 1,3-butadiene conversion. Kinetic studies showed that hydrogen has a kinetic reaction order of ∼1.2, indicating that hydrogen dissociation is the rate-determining step. Density functional theory (DFT) calculations revealed that butadiene strongly adsorbs on Pd_1 through a mono-π adsorption mode, distinctly different from the adsorption on Pd NPs or extended Pd surfaces, which favor butenes formation, especially 1-butene. Very interestingly, we found that the proximity oxygen atom is crucial for facilitating H_2 dissociation over the Pd_1 atom for sequential hydrogenation. The present work shed light on the adsorption mode induced selectivity change and the critical role of the proximity oxygen atom in SAC-catalyzed hydrogenation reaction.

2. Experimental

2.1. Catalyst synthesis

Firstly, graphene nanosheets (99.5%, Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences) was functionalized with isolated phenol groups using the Hummers method followed by thermal reduction in an argon inert gas at 1050 °C. The details were described in our previous work [10]. After that, Pd ALD was carried out in a viscous flow reactor (GEMSTAR-6™ Benchtop ALD, Arradiance) at 150 °C using palladium hexafluoroacety-

lacetate ($Pd(hfac)_2$, Sigma Aldrich, 99.9%) and formalin (Aldrich, 37% HCHO and 15% CH_3OH in aqueous solution) [17,18]. Ultrahigh purity N_2 (99.999%) was used as carrier gas at a flow rate of 200 ml/min. The $Pd(hfac)_2$ precursor container was heated to 65 °C, and the inlet manifold was held at 110 °C to avoid precursor condensation. The timing sequence was 120, 120, 60, and 120 sec for Pd $(hfac)_2$ exposure, N_2 purge, formalin exposure and N_2 purge, respectively. As a comparison, a Pd NP sample supported on graphene (Pd-NPs/graphene) was also prepared by annealing the Pd_1-O/graphene sample at 500 °C in helium atmosphere for 1 h.

2.2. Characterization

Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) measurements were taken on a JEM-ARM200F instrument (University of Science and Technology of China) at 200 keV. The Pd loadings were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

In situ XAFS measurements at Pd K-edge (24,350 eV) were performed in the fluorescence mode with the Si(3 1 1) monochromator at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF), China. The storage ring of SSRF worked at 3.5 GeV with a maximum current of 210 mA. Before the XAFS measurements, the Pd_1-O/graphene was in-situ pretreated with 10% O_2 balanced in helium at 150 °C for 1 h, and reduced with 10% H_2 balanced in helium at 150 °C for 1 h. The XAFS measurements were carried out after cooling down to room temperature in the helium atmosphere. After that the sample was further annealed at 500 °C in helium atmosphere for 1 h and recorded the XAFS spectrum at room temperature.

H_2-TPR was performed on an automated instrument of Micromeritics Autochem 2920 with a TCD detector. 100 mg Pd_1-O/graphene sample was loaded in a U-shaped quartz tube. Next, the sample was pretreated by 10% O_2/Ar at 200 °C for 1 h. After cooling the sample down to room temperature in the argon atmosphere, and stabilizing the baseline, TPR spectrum was then recorded by ramping the sample from 30 to 500 °C at a heating rate of 5 °C/min in 10% H_2/Ar.

2.3. Reaction test

In selective hydrogenation of 1,3-butadiene, the Pd_1-O/graphene SAC (25 mg, 0.27 wt%) diluted with 1 g of 60–80 mesh quartz chips was loaded in a 3/8 in. fixed-bed quartz-tube reactor. A K-type thermal couple protected by 1/8 in. quartz tube was inserted into the catalyst bed to monitor the catalyst temperature. The catalyst was pretreated by 10% O_2/Ar and 10% H_2/Ar at a flow rate of 25 ml/min at 150 °C for 30 min, respectively prior to the reaction test. Next, the catalyst was cooled down to room temperature under pure argon atmosphere, and the mixed gas consisting of 1.9% 1,3-butadiene and hydrogen (the concentration varied from 1.9% to 15.2%) balanced by argon at a flow rate of 25 ml/min, was injected into the catalyst bed. After that, the temperature was elevated to obtain different conversions in hydrogenation of 1,3-butadiene. To measure the reaction order of 1, 3-butdiene, we kept the hydrogen concentration constant at 7.6% while changing the 1,3-butadiene concentrations from 1.9% to 7.6%. The reaction products were analyzed using an online gas chromatography equipped with a FID detector and a capillary column (ValcoPLOT VP-Alumina, 50 m x 0.53 mm) after stabilizing in the feed gas for 2 h.

2.4. H-D exchange reaction

80 mg of 0.25 wt% Pd_1-O/graphene catalyst was used in the H-D exchange reaction. The feed gas consists of 5% deuterium (D_2), 4.7%