The precise decoration of Pt nanoparticles with Fe oxide by atomic layer deposition for the selective hydrogenation of cinnamaldehyde

Qingmin Hu [a,b], Sen Wang [b,c], Zhe Gao [b,*], Yunqin Li [b,c], Qian Zhang [b,c], Qun Xiang [a,*], Yong Qin [b,*]

[a] NEST Lab, Department of Chemistry, Shanghai University, Shanghai 200444, PR China
[b] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China
[c] Graduate University of Chinese Academy of Sciences, Beijing 100039, PR China

ABSTRACT

The decoration of noble metal-based catalysts with metal oxides can improve their catalytic performance for the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol (COL) due to the interaction between the noble metal and metal oxides. Here, we used atomic layer deposition (ALD) to decorate Pt nanoparticles precisely with Fe oxides. The selectivity to COL increased from 45% for the bare Pt catalyst to 84% for the Pt-based catalyst after 30 cycles of decoration with Fe oxide by ALD. A series of characterizations demonstrated that the precise blocking of low coordinated Pt sites with Fe oxide by ALD, generating Pt-FeO$_x$ interfacial perimeter sites, and the interaction between the Pt nanoparticles and Fe oxide led to high selectivity to COL. This precise decoration and the formation of interfacial perimeter sites by ALD provide a promising route for the design of advanced catalysts.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The selective hydrogenation of the carbonyl bond (C=O) of α-β unsaturated aldehydes to form the corresponding unsaturated alcohols has caught the attention of researchers because these products are widely used in industry [1–3]. Cinnamaldehyde (CAL) is a typical unsaturated aldehyde [4–7]. Because of the competitive hydrogenation of the C=C and C=O bonds, the products of the hydrogenation of CAL include COL, hydrocinnamaldehyde (HCAL) and 3-phenylpropanol (HCOL) (Scheme 1). COL is widely used in fragrances, drugs and other chemicals. Pt-based catalysts are usually used in the selective hydrogenation of CAL for the preparation of COL. Significant efforts have been made to promote the selective hydrogenation of the C=O bond by Pt-based catalysts while hindering the hydrogenation of the C=C bond [3,8,9]. There are several factors that influence the catalyst selectivity to COL, such as the interfacial perimeter sites, the strong metal-support interaction (SMSI) [10,11], the geometry and size of the catalytic metal nanoparticle [11–15], and the electronic state of the catalytic metal

surface atoms [14,16,17]. The interfacial perimeter sites play a vital role in this hydrogenation reaction [18].

In recent decades, many researchers have found that different sites on the Pt nanoparticles surface influence the adsorption modes of the reactant [17,19,20]. DFT calculation demonstrated that flat surfaces, such as Pt (111), adsorb the unsaturated aldehyde in a terminal C=O mode. This mode leads the preferential terminal aldehyde to be reduced to unsaturated alcohol. Pt (100) prefers the adsorption of both C=O and C=C. Low coordinated sites (such as steps, edges, corners, and defect sites) favour π interactions with C=C, accounting for unselective product formation [21]. Smaller nanoparticles possess more low coordinated sites such as corners and edges but fewer facets than larger nanoparticles [14,22]. Decorating the low coordinated Pt sites with other species and selectively forming interfacial perimeter sites would be interesting as a way to change the selectivity to COL.

Adding another species (promoter), such as Co [17,23] or Fe [23], to Pt-based catalysts can improve their selectivity to COL. The unsaturated aldehydes adsorbed more strongly via the C=O bond in a di-σ mode at the resulting interfacial perimeter sites [24]. Furthermore, electron transfer between the added species and the Pt nanoparticles was observed [25]. The selective blockage of a metal nanoparticle surface by another species is an effective method to improve the catalytic selectivity and has been widely studied [26,27].

* Corresponding authors.
  E-mail addresses: gaozhe@sxicc.ac.cn (Z. Gao), shinexq@shu.edu.cn (Q. Xiang), qinyong@sxicc.ac.cn (Y. Qin).
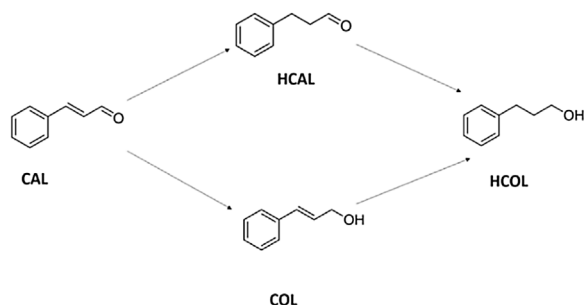
Scheme 1. Reaction pathways of cinnamaldehyde hydrogenation.

Atomic layer deposition (ALD) is a powerful technique for depositing nanoparticles or thin films and has outstanding advantages, including precise control of size and thickness and excellent uniformity [28–30]. ALD is also an advanced catalyst design method for improving catalytic performance [31–33]. Lu and co-workers reported that Al_2O_3 ALD was able to block low coordinated metal sites while leaving (111) facets available for the catalysis of Pd [34] (or Cu, Pt [35]) nanoparticles. In this work, different numbers of cycles of ALD Fe oxide were used to precisely decorate Pt nanoparticles. Low coordinated Pt sites were blocked. The resulting interfacial perimeter sites are more beneficial to the hydrogenation of the C=O bond than low coordinated Pt sites, increasing the selectivity to COL. After the decoration of Pt nanoparticles with ALD Fe oxide, the selectivity to COL improved from 45% to 84%.

2. Experimental Method

2.1. Catalyst synthesis

Prior to ALD, Al_2O_3 (aluminium oxide, 40–50 nm, 32–40 m^2/g, NanoDur, 99.5%, Alfa Aesar Co., Ltd.) powders were dispersed in ethanol by ultrasonic agitation for ten minutes. The suspension was dropped onto quartz wafers and dried in air. Pt nanoparticles were deposited onto the Al_2O_3 supports by a hot-wall, closed-chamber ALD reactor. N_2 (99.999%) was used as carrier gas. The precursors of Pt were (methylcyclopentadienyl)trimethylplatinum ($MeCpPtMe_3$, Strem Chemicals, 99%) and ozone (O_3). O_3 acts as an oxidant and enables growth over a wide temperature range. The deposition temperature was 270 °C, and the $MeCpPtMe_3$ was kept at 60 °C. The pulse, exposure, and purge time for the $MeCpPtMe_3$ precursor were 0.5, 10 and 20 s, and for O_3, 1, 10 and 20 s, respectively. After the deposition of Pt nanoparticles, Fe_2O_3 ALD was subsequently deposited with ferrocene (Aladdin Chemistry Co. Ltd. 99%) and O_3 as precursors at the same temperature as for Pt ALD. The ferrocene was kept at 90 °C. The pulse, exposure, and purge time for the ferrocene precursor were 0.8, 8 and 20 s, and for O_3, 0.3, 8 and 20 s, respectively. Ultimately, the catalysts were transferred into a tube furnace and reduced at 400 °C in a H_2/Ar atmosphere for 2 h.

In this paper, the reduced Pt/Al_2O_3 catalyst produced with 30 cycles of Pt deposition is designated Pt30. The Pt-based catalysts decorated with different numbers of cycles of Fe oxide deposition by ALD are designated Pt30Fex, where x is the number of Fe oxide ALD cycles (10, 20, 30, 40 and 75, respectively). These Pt30 and Pt30Fex catalysts before reduction are designated un-Pt30 and un-Pt30Fex, respectively.

For comparison, catalysts were also prepared by traditional impregnation methods. First, Pt30 was prepared by ALD, and then the powders were impregnated with Fe(NO)$_3$•9H$_2$O in solution (pH = 3) for 10 minutes with different Fe contents of 0.5%, 0.85%, and 5%. Afterwards, the solution was dried at 110 °C for 2 h and subsequently calcinated at 500 °C for 2 h in static air. The sample was also reduced at 400 °C in a H_2/Ar (5%/95%) atmosphere for 2 h. The

obtained catalysts were designated Pt30-0.5Fe-IWI, Pt30-Fe-IWI, and Pt30-5Fe-IWI, respectively.

2.2. Catalyst characterization

The contents of Pt and Fe in the catalysts were determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES). Transmission electron micrographs (TEM) and high-resolution TEM (HRTEM) images were acquired with a JEOL-2100F microscope.

XRD patterns were collected on a Bruker D8 Advance X-ray diffractometer using a Cu Kα source. The N_2 sorption measurements were performed using a Micromeritics Tristar 3000 at 77 K. Prior to measurement, the samples were heated at 473 K for 1 h under vacuum to remove physisorbed water. The Brunauer−Emmett−Teller (BET) surface areas were estimated over a relative pressure (P/P$_0$) range of 0.04–0.32.

Temperature programmed reduction (TPR) experiments were performed with an Auto-Chem 2920 instrument, using a 50 mg sample under a 50 mL·min^{-1} H_2 (10%)/Ar flow with a heating rate of 10 °C·min^{-1} from room temperature to 700 °C.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) data on CO adsorption were collected on a Bruker Vector 22 spectrometer with a DTGS detector. Before the experiments, the sample in the cell was dried and reduced in H_2/Ar at 400 °C for 2 h. Subsequently, the cell was cooled to room temperature (20 °C), and then the CO adsorption was carried out using CO/Ar (5%/95%) until saturated. The flow of Ar was maintained for 30 minutes to remove physically adsorbed CO, and finally, the CO chemisorption spectra were recorded with a resolution of 2 cm^{-1} at room temperature.

X-ray photoelectron spectroscopy (XPS) data were taken on an ES-300 photoelectron spectrometer (KRATOS Analytical) using an Al Kα source (1486.6 eV).

The pulse CO chemisorption experiments on the catalysts were carried out on an Auto Chem 2920 instrument equipped with a thermal conductivity detector (TCD). Before testing, the catalyst was reduced at 400 °C for 2 h and then cooled in Ar to room temperature (298 K).

Pt L-edge absorption spectra were obtained at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF), Shanghai Institute of Applied Physics (SINAP), China, operated at 3.5 GeV. A Si (111) double-crystal monochromator was used to reduce the harmonic component of the monochrome beam. Pt foil and PtO$_2$ were used as reference samples and measured in transmission mode. The Pt-based catalysts were measured in fluorescence mode.

2.3. Hydrogenation reaction

The catalytic hydrogenation of CAL (J&K Chemical, 99%) was performed in an autoclave of 100 mL with a temperature controller. In each experiment, 45 mL ethanol, 150 μL CAL and 30 mg catalyst were loaded into the reactor. The reactor was sealed and purged with purified hydrogen 3 times to remove air, and then pressurized to 2 MPa at room temperature. Subsequently, the reactor was heated to 60 °C and stirred at 700 rpm.

Disposable syringe filters were used to separate the catalyst. The liquid products collected by continuous sampling were analysed by gas chromatography-mass spectrometry (GC-MS, Agilent Technologies 7890A-5795C) with a capillary column (HP-5, 30 m × 0.25 mm × 0.25 μm).