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# Activity and Selectivity in Nitroarene Hydrogenation over Au Nanoparticles on the Edge/Corner of Anatase

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**ABSTRACT:** Highly selective hydrogenation of molecules containing more than one reducible groups is always challenging. Here we report an efficient strategy for rational preparation of highly selective gold-based catalysts in hydrogenation of substituted nitroarenes by positioning gold nanoparticles on the edge/corner sites of anatase. Mechanistic studies reveal that the catalyst with gold nanoparticles on the edge/corner sites of anatase could form unique sites for selective adsorption and activation of nitro groups, thus leading to high activity and selectivity. This strategy for preparation of supported gold catalysts opens a new door for design of highly efficient heterogeneous catalysts in the future.

KEYWORDS: gold nanoparticle, nitrobenzene hydrogenation, high activity, anatase, adsorption, selectivity

### **1. INTRODUCTION**

The metal-catalyzed hydrogenations with molecular hydrogen have been regarded as a great discovery in the production of fine chemicals and pharmaceuticals.1-9 In these reactions, when more than one reducible groups are present on substrate molecules, selective hydrogenation of the target group is challenging because the sidereactions easily occur on the non-target groups.10-20 One efficient approach for solution of this problem is to poison/block some of the atoms on the catalyst surface by additives such as quinoline, carbon monoxide, thiol ligands, and metal-based modifiers.<sup>21-25</sup> Because numerous studies have demonstrated the differences in catalytic activity or selectivity when reactions occurs on different sites of the metal nanocrystals,<sup>26-28</sup> poisoning/blocking the sites for undesired reactions could achieve encouraging progress for improving catalytic selectivities.<sup>29,30</sup> A prominent example is the industrial Lindlar catalyst. However, in most of these cases, catalytic activities are remarkably reduced due to poisoning the catalysts.<sup>21,22</sup> In addition, leaching of these additives in the catalytic systems is difficult for the catalyst recycling. Therefore, it is strongly desirable to simultaneously enhance the catalytic activity and selectivity in the hydrogenation.

Hydrogenation of substituted nitroarenes is chosen as a model in this work because these hydrogenated products are industrially important intermediates for the formation of fine chemicals and high-performance rubbers and polymers.<sup>2,31-38</sup> Recently, it is reported that TiO<sub>2</sub> supported Au nanocatalysts (Au/TiO<sub>2</sub>) are successful for selective hydrogenation of substituted nitroarenes to anilines by selectively adsorption of the nitro groups.<sup>2,38</sup> This discovery leads to a series of investigations in this field, but the poor activities of Au/TiO<sub>2</sub> catalysts still hinder the practical applications.<sup>2,31,35,36</sup> An attractive strategy for enhancing catalytic activities of the Au/TiO<sub>2</sub> catalysts is to rationally design their structures, and successful examples are preparation of highly active catalysts for the water-gas shift and various oxidations,<sup>39-40,41-</sup> <sup>44</sup> but it is still not successful for enhancement of catalytic activity in the nitroarene hydrogenation by adjusting the structure of the Au/TiO<sub>2</sub> catalysts.

To understand the dependence of the Au/TiO2 structure on the activity in the nitroarene hydrogenation, a theoretical simulation for the adsorption of nitrobenzene molecule on the Au/TiO<sub>2</sub> with different structures has been studied. Very interestingly, it is observed that the adsorption of the nitrobenzene on the edge/corner sites of TiO<sub>2</sub> support is stronger than that on the (101) facet of TiO<sub>2</sub> (See the details in Figure S1). Based on the wellknown knowledge that the adsorption is a very important step in hydrogenation of nitroarenes,38 it is suggested that the Au nanoparticles loaded on the edge/corner sites of TiO<sub>2</sub> support (Au/TiO<sub>2</sub>-EC) could improve the catalytic activities. As we expected, when the Au/TiO<sub>2</sub>-EC is used to catalyze hydrogenation of 3nitrostyrene, the turnover frequency of 279 h<sup>-1</sup> is obtained. This value is much higher than those (<173 h<sup>-1</sup>) of the conventional Au nanocatalysts.<sup>35</sup> More importantly, the chemoselectivity to 3-aminostyrene could reach as high as 99.0%. Our study reveals that the specific loading methodology might open a new door for design and preparation of highly efficient catalysts with simultaneous activities and selectivities in the hydrogenations.

#### 2. EXPERIMENTAL SECTION

**2.1 Materials.** All reagents were of analytical grade and used as purchased without further purification.

2.2 Synthesis. The anatase support Au nanocatalyst with Au nanoparticles mostly loaded on the edge/corner sites of anatase (Au/TiO<sub>2</sub>-EC) was synthesized according to our previous work.<sup>44</sup> As a typical run for synthesizing Au/TiO<sub>2</sub>-EC, 250 mg of polyvinylpyrrolidone (PVP, K13-K18, average molecular weight at ~10,000) was added into HAuCl<sub>4</sub> solution (0.55 mmol of Au and 300 ml of water) and stirred at 0 °C for 1 hour. Then NaBH<sub>4</sub> solution (400 mg of NaBH<sub>4</sub> in 20 ml of water) was rapidly added under vigorous stirring at o °C for another 1 hour. Followed by adding 10 g of anatase, the mixture was further stirred at 40 °C under vacuum to evaporate the water. Finally, the solid powder was washed with a large amount of water for many times and calcined at 400 °C for 4 hours in oxygen with programmed increase of temperature (from room temperature to 300°C at 1°C/min, after 2 h, increase to 400 °C at 1°C/min) to remove PVP. After washing with NaBH<sub>4</sub> solution for 8 h at room temperature, the Au/TiO<sub>2</sub>-EC sample with Au content at 0.91 wt% was obtained.

The conventional Au nanocatalyst with Au nanoparticles mostly loaded on the anatase facet sites (Au/TiO<sub>2</sub>-Con) was synthesized by deposition-precipitation method. As a typical run, 10 g of anatase was added to 500 ml of HAuCl<sub>4</sub> (0.55 mmol of Au) and urea (50 mmol) solution. After stirring at 90 °C for 4 hours in a closed reactor kept away from the light, the liquid mixture was cooled in an ice bath at 0 °C, followed by adding NaBH<sub>4</sub> solution (400 mg of NaBH<sub>4</sub> in 20 ml of water). Finally, the solid sample was filtrated and washed with a large amount of water, dried at 100 °C for 12 hours, and calcined at 400 °C for 4 hours. After washing with NaBH<sub>4</sub> solution for 8 h at room temperature, the Au/TiO<sub>2</sub>-Con sample with Au content at 0.87 *wt*% was obtained.

2.3 Characterization. XPS spectra were performed on a Thermo ESCALAB 250with Al Ka radiation at  $h = 90^{\circ}$  for the X-ray sources; the binding energies were calibrated using the C1s peak at 284.9 eV. IR spectrawere recorded using a Nicolet NEXUS 670 FT-IR spectrometer equipped with a MCT detector and ZeSe windows and a high temperature reaction chamber. The nitrobenzene steam was introduced into the system by Ar flow. The content of Au was determined from inductively coupled plasma (ICP) with a Perkin-Elmer Plasma 40 emission spectrometer. The position of Au nanoparticles was demonstrated by high-resolution transmission electron microscopy (HR-TEM) over a JEOL JEM-3000F microscope equipped with a field-emission gun. By analyzing more than 100 Au nanoparticles randomly selected in the HR-TEM images for each sample, we confirm that 86% of the Au nanoparticles of Au/TiO<sub>2</sub>-Con sample are located on the (101) surface of anatase, while more than 75% of the Au nanoparticles of Au/TiO<sub>2</sub>-EC are on the edge/corner sites of anatase support. These detailed information in catalyst structures of Au/TiO<sub>2</sub>-EC and Au/TiO<sub>2</sub>-Con was included in our previous work.44

**2.4 Catalytic tests.** The hydrogenation reactions were performed in a high-pressure autoclave with a magnetic stirrer (1200 rpm). Typically, the substrate, catalyst, and solvent were mixed in the reactor and stirred for 15 min at room temperature. Then, pure hy-

drogen was introduced and kept at a desired pressure (measured at the reaction temperature) and the reaction system was heated to a given temperature (measured with a thermometer in an oil bath). After the reaction, the product was taken out of the reaction system and analyzed by gas chromatography (GC-14C, Shimadzu, using a flame ionization detector) with a flexible quartz capillary column coated with OV-17 or FFAP. The recyclability of the catalyst was tested by separating it from the reaction system by centrifugation, washing with a large quantity of methanol, and drying at 80 °C for 6 hours. In the recyclable test of Au/TiO<sub>2</sub>-EC, the Au concentration in the liquor is less than 5 ppb by ICP analysis after separating the used solid catalyst, indicating that no Au leaching occurred during the reaction.

#### **3. RESULT and DISCUSSION**

**3.1 Kinetic study.** The Au nanoparticles supported on the edge/corner sites of anatase were synthesized according to the literature (Au/TiO<sub>2</sub>-EC).<sup>44</sup> For comparison, the control catalyst of conventional Au/TiO<sub>2</sub> with Au nanoparticles mostly attached on the facet of TiO<sub>2</sub> support was also synthesized, denoted as Au/TiO<sub>2</sub>-Con. The Au loading were established to be 0.91 and 0.87 *wt%* by inductively coupled plasma (ICP) analysis, respectively.



**Figure 1.** Kinetic studies in nitrobenzene hydrogenation over Au catalysts. (A) TOFs of the Au/TiO<sub>2</sub>-EC and Au/TiO<sub>2</sub>-Con in hydrogenation of nitrobenzene. (B) Experimental points correlating the inverse of the absolute temperature (1/T) with the initial reaction rates (ln  $r_0$ ) over the Au/TiO<sub>2</sub>-EC and Au/TiO<sub>2</sub>-Con catalysts. (C) Dependences of reaction rate on nitrobenzene concentration over the Au/TiO<sub>2</sub>-EC and Au/TiO<sub>2</sub>-Con catalysts. (D) Dependences of reaction rate on hydrogen pressure over the Au/TiO<sub>2</sub>-EC and Au/TiO<sub>2</sub>-Con catalysts.

We start from a kinetic study on the hydrogenation of nitrobenzene over the Au-based catalysts. The anatase support without Au species is inactive for the reaction. By studying the turnover frequencies (TOFs) according to the nitrobenzene conversion at the start of each reaction, it is found that the Au/TiO<sub>2</sub>-EC always exhibited higher TOF values than Au/TiO<sub>2</sub>-Con at various reaction 1

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temperatures (Figure 1A), implying the high activity. Based on the initial reaction rate ( $r_o$ ) values at different reaction temperature (Figure S2), the apparent activation energies ( $E_a$ ) of Au/TiO<sub>2</sub>-EC and Au/TiO<sub>2</sub>-Con are calculated to be ~26 and ~40 KJ mol<sup>-1</sup>, respectively (Figure 1B). The different  $E_a$  values indicate that the conversion of nitrobenzene over Au/TiO<sub>2</sub>-EC is much easier than that over Au/TiO<sub>2</sub>-Con.

Furthermore, the dependences of  $r_o$  values on nitrobenzene concentration and gaseous hydrogen pressure were performed to understand the kinetic reaction orders. Very clearly, the Au/TiO<sub>2</sub>-EC always exhibits higher  $r_o$  values than Au/TiO<sub>2</sub>-Con under either different nitrobenzene concentration or different hydrogen pressure (Figures 1C and 1D). Importantly, at low nitrobenzene concentration (<0.05 mol L<sup>-1</sup>), the rates over Au/TiO<sub>2</sub>-Con increase more significantly than those of Au/TiO<sub>2</sub>-EC, yielding the kinetic orders for nitrobenzene concentration at 0.27 and 1.11 for Au/TiO<sub>2</sub>-EC and Au/TiO<sub>2</sub>-Con, respectively. Under constant concentration of nitrobenzene, the reaction rates over Au/TiO<sub>2</sub>-Con is constant with increasing the hydrogen pressure (Figure 1D), indicating the zero kinetic order. In this case, the activation of nitrobenzene acted as a rate control step over Au/TiO<sub>2</sub>-Con in the hydrogenation of nitrobenzene. In comparison, the rates over Au/TiO<sub>2</sub>-EC increase with the hydrogen pressure, giving the reaction kinetic order at 0.85. This phenomenon indicates that the Au/TiO<sub>2</sub>-EC breaks through the limitation of nitrobenzene activation, exhibiting hydrogen activation as a control step.

By the kinetic studies, it is identified unequivocally that the Au/TiO<sub>2</sub>-EC is more catalytically efficient than the Au/TiO<sub>2</sub>-Con in the hydrogenation of nitrobenzene (Figure S3). Considering that the weak transfer limitation of the reaction substrates on these nano-sized anatase supported Au catalysts, the distinguishing apparent  $E_a$  values and reaction kinetic orders suggest that the Au/TiO<sub>2</sub>-EC catalyst should have superior ability than Au/TiO<sub>2</sub>-Con in activating nitro groups.



**Figure 2.** (A) IR spectra of nitrobenzene adsorbed on the Au/TiO<sub>2</sub>-EC, Au/TiO<sub>2</sub>-Con, and anatase; (B) IR spectra of the adsorbed nitrobenzene on the Au/TiO<sub>2</sub>-EC during the

TPD process. Desorption conditions: (a) 50 °C, 10 min, (b) 50 °C, 30 min, (c) 100 °C, 10 min, (d) 100 °C, 20 min, (e) 100 °C, 30 min, (f) 150 °C, 10 min, (g) 150 °C, 20 min, (h) 150 °C, 30 min, (i) 200 °C, 10 min, (j) 200 °C, 20 min, (k) 200 °C, 30 min, (l) 300 °C, 10 min, (m) 300 °C, 20 min, and (n) 300 °C, 30 min; (C) Changes in IR band intensities during the TPD process.

**3.2** Nitro group-adsorption IR. It has been reported that IR spectroscopy is powerful for understanding the adsorption of nitro molecules on solid support.<sup>38,45</sup> Therefore, in order to understand the interaction between nitrobenzene and catalysts, we conducted the FT-IR spectra of nitrobenzene adsorbed on Au/TiO<sub>2</sub>-EC, Au/TiO<sub>2</sub>-Con, and anatase. The Au/TiO<sub>2</sub>-EC gives strong absorbance bands at 1527, 1491, and 1349 cm<sup>-1</sup> assigned to the nitro groups (Figure 2A). The bands at 1527 and 1349 cm<sup>-1</sup> have already been definitely understood as the asymmetric stretching(v<sub>asym</sub>) vibration frequency of nitro group adsorbed on Ti-OH group and symmetric stretching(v<sub>sym</sub>) vibration frequency of nitro group adsorbed on the electron-rich surface Ti atoms,



**Figure 3.** FT-IR spectra of the nitrobenzene adsorbed on the (A) Au/TiO<sub>2</sub>-Con and (B) anatase. Desorption temperature at (a) 50 °C, (b) 100 °C, (c) 150 °C, (d) 200 °C, and (e) 250 °C.



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**Figure 4.** (A) IR spectra of the nitrobenzene adsorbed on  $Au/TiO_2$ -EC under flowing  $H_2/Ar$  at 90 °C for (a) 0 min, (b) 2 min, (c) 3 min, (d) 9 min, and (e) 10 min; (B) IR spectra of the nitrobenzene adsorbed on Au/TiO\_2-EC under flowing Ar at 90 °C for (a) 0 min and (b) 30 min.

respectively.<sup>36,45</sup> Notably, the  $v_{sym}$  band at 1349 cm<sup>-1</sup> is undetectable on the Au/TiO<sub>2</sub>-Con and anatase (Figure 2A), due to the lack of electron-rich Ti atoms, as confirmed by the XPS spectra (Figure S4).

Additionally, on the IR spectrum of nitrobenzene on the Au/TiO<sub>2</sub>-EC, the band at 1491 cm<sup>-1</sup> (Figure 2A), which is rarely reported yet, is reasonably assigned to another asymmetrical adsorption type of nitro group on the Au/TiO<sub>2</sub>-EC. It is worth noting that the band of nitro group at 1491 cm<sup>-1</sup> has significant red shift from the conventional  $v_{asym}$  band of nitro group (1527 cm<sup>-1</sup>), indicating that the N=O bonds are significantly weaken by

interacting with the Au/TiO<sub>2</sub>-EC catalyst. Therefore, the 1491-cm<sup>-1</sup> band should be favorable for the hydrogenation of nitro groups.

Figure 2B shows the FT-IR spectra of the adsorbed nitrobenzene on the Au/TiO<sub>2</sub>-EC during the temperature programmed desorption (TPD) process in flowing Ar. Correspondingly, the spectral changes of the  $v_{sym}(1349)$ cm<sup>-1</sup>), v<sub>asym</sub>(1491 cm<sup>-1</sup>), and v<sub>asym</sub> (1527 cm<sup>-1</sup>) bands in intensity are given in Figure 2C. Clearly, the v<sub>sym</sub> (1349 cm<sup>-1</sup>) and v<sub>asym</sub> (1527 cm<sup>-1</sup>) bands exhibit significant decrease in intensity with increasing the desorption temperature. At 150 °C, the extremely weak v<sub>sym</sub>(1349 cm<sup>-1</sup>) and v<sub>asym</sub>(1527 cm<sup>-1</sup>) bands confirm that most of the nitro groups are desorbed from the corresponding sites (Figure 2B-h). At the same time, the vasym(1491 cm<sup>-1</sup>) band becomes stronger by increasing the temperature from 50 to 150 °C (Figures 2B and 2C), which is different from the general phenomenon observed on the bands of 1349 and 1527 cm<sup>-1</sup>. This phenomenon might be attributed to the transfer of nitrobenzene molecules, which were desorbed from the electron Ti atoms and/or Ti-OH groups by increasing temperature, and re-adsorbed asymmetrically on the unique strong adsorption sites, leading to the enhancement in the vasym(1491 cm<sup>-1</sup>) band intensity. Notably, further increasing the temperature (>200 °C) could also lead to a decreased intensity of the vasym(1491 cm<sup>-1</sup>) band, but obvious peak could still be detected even at a high temperature of 300 °C (Figure 2B-n). These obser-



**Figure 5.** (A) The Fukui Function distribution of contour (a)  $Au_{13}$ , (b)  $Au_{13}$ /TiO<sub>2</sub> model with no oxygen vacancy (Relation to Au/TiO<sub>2</sub>-con), and (c)  $Au_{13}$ /TiO<sub>2</sub> with oxygen vacancy (Relation to Au/TiO<sub>2</sub>-EC, the contour iso value is 0.025). The yellow density indicates that the Fukui Function at that site is positive  $f^0(r) > 0$ , while the blue color density indicates that the Fukui Function at that site is negative  $f^0(r) < 0$ ; (B) CO-adsorption IR spectra of the Au/TiO<sub>2</sub>-EC and Au/TiO<sub>2</sub>-Con; (C) The zoomed-in image of the most energetic favourable structure of nitrobenzene attached on  $Au_{13}$ /TiO<sub>2</sub> model with one oxygen vacancy.

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59 60 vations indicate unique stability of the 1491 cm<sup>-1</sup> species due to the strong adsorption of nitro groups. In contrast, the IR bands of nitrobenzene adsorbed on Au/TiO<sub>2</sub>-Con (Figure 3A) and TiO<sub>2</sub> (Figure 3B) are very weak after desorption at 150 °C, due to the lack of strong adsorption sites for nitro groups.

Importantly, after introduction of H<sub>2</sub> to the Au/TiO<sub>2</sub>-EC adsorbed nitrobenzene, the intensity of the  $v_{asym}(1491 \text{ cm}^{-1})$  band decreased more immediately and significantly than those of  $v_{asym}$  (1527 cm<sup>-1</sup>) and  $v_{sym}$  (1349 cm<sup>-1</sup>) in the IR spectra (Figure 4A), which is different from the phenomenon during the desorption process in following Ar under the same temperature (Figure 4B). These results might suggest that the nitro groups on  $v_{asym}(1491 \text{ cm}^{-1})$  band are favorable to be reduced, because these nitro groups are highly activated by the strong adsorption, which could explain the origin of higher activity of the Au/TiO<sub>2</sub>-EC than the Au/TiO<sub>2</sub>-Con.

**3.3 DFT simulations.** To further understand the adsorption behavior of nitrobenzene on the catalysts, we performed density functional theory (DFT) simulations to understand the catalytic mechanism in principle. The computational models with  $Au_{13}$  clusters supported on anatase were built and optimized (Figure S5). According to our previous study in Au-anatase nanostructure, the model with  $Au_{13}$  on the edge/corner sites of anatase, which simulates  $Au/TiO_2$ -EC catalyst, is favorable to produce oxygen vacancies on the Au-anatase interface due to the strong interaction between Au and Ti.<sup>44</sup> In contrast, the model of  $Au_{13}$  on the {101} facet of anatase, which simulates  $Au/TiO_2$ -Con catalyst, has weak Au-Ti

interaction. In these optimized models, we have implemented Fukui function as the principle factor to illustrate the potential possibility of the models for adsorbing/interacting with nitro group, because the Fukui Function was defined as the first derivative of the electron density at a position  $r.^{46,47}$  As shown in Figure 5A-a, the Fukui Function of Au<sub>13</sub> itself is symmetric. However, once attached on the anatase nanosupport, the Fukui Function of Au<sub>13</sub> presented distinguished changes in terms of the distribution, which proves the anatase support introduced significant impact on Au nanoparticle (Figure 5A-b). Interestingly, the model with oxygen vacancy exhibits a more electrophilic region around the TiO<sub>2</sub>-Au<sub>13</sub> interface (Figure 5A-c). To experimentally confirm this on the synthesized catalysts, we perform COadsorption IR spectra on Au/TiO<sub>2</sub>-EC and Au/TiO<sub>2</sub>-Con samples, because CO is known as an electron-rich molecule and sensitive to determine the electronic structure of the solid surfaces. As shown in Figure 5B, the liner CO vibrational frequency on the Au/TiO<sub>2</sub>-EC was 2109 cm<sup>-1</sup>, 25 cm<sup>-1</sup> of shift higher than that of the Au/TiO<sub>2</sub>-Con (2084 cm<sup>-1</sup>). This blue shift indicates the stronger binding of CO on the Au/TiO<sub>2</sub>-EC than the Au/TiO<sub>2</sub>-Con, because the CO benefits more to adsorb on the electrophilic sites.48,49

Furthermore, we introduce a nitrobenzene molecule to the model of  $Au_{13}$  on the edge/corner sites of anatase. By attaching nitrobenzene on different positions of the model, we found that the most energetic favorable adsorption for nitrobenzene can occur near the oxygen vacancy on the Au-TiO<sub>2</sub> interface (Figure S6B). The nitro

Substrate	Catalyst	Conditions <sup>b</sup>	Conv.	Sel. <sup>c</sup>	
			(%)	(%)	
3-nitrostyrene	Au/TiO <sub>2</sub> -EC	90 °C/10 bar/4.5 h	99.0	99.0	
	Au/TiO <sub>2</sub> -Con	90 °C/10 bar/4.5 h	55.5	93.3	
	Au/TiO <sub>2</sub> -Con	90 °C/10 bar/7 h	71.1	93.1	
	Au/TiO <sub>2</sub>	120 °C/9 bar/6 h	98.5	<b>95.9</b> <sup>d</sup>	
	Au-Pd/TiO <sub>2</sub>	120 °C/9 bar/0.03 h	99.5	$\mathbf{O}^{\mathrm{d}}$	
2-chloro-4-nitrophenol	Au/TiO <sub>2</sub> -EC	100 °C/10 bar/2 h	98.3	99.5	
	Au/TiO <sub>2</sub> -Con	100 °C/10 bar/2 h	60.0	91.0	
2-nitroacetophenone	Au/TiO <sub>2</sub> -EC	100 °C/10 bar/2 h	99.3	99.0	
	Au/TiO <sub>2</sub> -Con	100 °C/10 bar/2 h	67.3	97.0	

Table 1. Catalytic data in the hydrogenation of different molecules over various catalysts.<sup>a</sup>

<sup>a</sup> Reaction conditions: 0.8 mmol of nitrobenzene, 40 mg of catalyst, 3 ml of toluene, the molecular formula of substrates, and products are presented in Scheme S1; <sup>b</sup> Reaction temperature/H<sub>2</sub> pressure/reaction time; <sup>c</sup> Selectivity to the corresponding substituted aniline product; <sup>d</sup> The data are from Ref. 2.

group of nitrobenzene interacts with one Au atom via forming a Au-O interaction (Figure S7). Meanwhile, the Ti atom nearby also interacts with this oxygen atom, which leads to a noticeable lengthening of the N-O bond (Figure 5C). It is important to remark that the oxygen vacancy locates right next to this Au atom. There is also a distortion of the benzene ring due to the interaction between some of the carbon atoms and the Au atoms upper body. It turns out this attaching manner leaves the other oxygen atom of nitro group easily being attacked by the coming hydrogen species, which initiates the hydrogenation reaction to occur at the attaching site (See details in Figures S6 and S7). Meanwhile, this adsorption behavior is unavailable when the oxygen vacancy is artificially eliminated on the catalyst model. Such changes in simulation indicate the important role of catalyst structure. Combining with the results in nitrobenzene adsorption-IR spectra, it could be proposed that the strong adsorption and activation of nitro group on the Au/TiO<sub>2</sub>-EC lead to the high catalytic activity in hydrogenation of nitrobenzene.

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3.4 Hydrogenation selectivity. The hydrogenation of 3-nitrostyrene was performed to study the catalytic selectivity, because the vinyl groups are very active in the hydrogenation. Although Au nano catalysts have been reported to exhibit more than 90% selectivity in the hydrogenation of 3-nitrostyrene to 3-aminostyrene,<sup>2</sup> it is surprising to observe that the selectivity could be further improved over the Au/TiO2-EC, giving the 3aminostyrene selectivity at 99.0%, as shown in Table 1. Under the same reaction conditions, the Au/TiO<sub>2</sub>-Con gives really lower conversion and selectivity at 55.5 and 93.3%, respectively. This phenomenon is reasonably attributed to the selectively and strongly adsorbing the nitro group of 3-nitrostyrene molecule on Au/TiO<sub>2</sub>-EC (Figures S8-S11). In addition, the chemoselective reduction of nitro group in the presence of carbonyl, phenol, and chlorine groups has been studied through the hydrogenation of 2-chloro-4-nitrophenol and 2nitroacetophenone (Scheme S1). In these cases, the Au/TiO<sub>2</sub>-EC always exhibits excellent selectivity to the

corresponding amines at 99.0-99.5%, which are much higher than those (91.0-97.0%, Table 1) over the Au/TiO<sub>2</sub>-Con catalyst, indicating the excellent selectivity of Au/TiO<sub>2</sub>-EC catalyst. Based on these results, one can assume that the Au/TiO<sub>2</sub>-EC is more specific than Au/TiO<sub>2</sub>-Con to catalyze the reduction of nitro group due to the strong adsorption of nitro group on Au/TiO<sub>2</sub>-EC, as confirmed by the IR study. To check this hypothesis, hydrogenation of various groups were carried out separately by employing as substrates. As summarized in Table 2, both Au/TiO<sub>2</sub>-EC and Au/TiO<sub>2</sub>-Con are active for the hydrogenation of all substrates. When nitrobenzene, styrene, acetophenone and chlorobenzene were physically mixed as substrate, the Au/TiO<sub>2</sub>-EC is only active for hydrogenation of the nitrobenzene, where the hydrogenation of other groups (e.g. -Cl, -C=O, -C=C) are prevented in the complete hydrogenation reactions. In comparison, the Au/TiO<sub>2</sub>-Con is still active for hydrogenation of the nitrobenzene, styrene, and acetophenone (Table 2). These results indicate the obvious advantage of the Au/TiO<sub>2</sub>-EC in selective hydrogenations, compared with the Au/TiO<sub>2</sub>-Con.

**3.5 Recyclability test.** In the hydrogenation of 3nitrostyrene, the Au/TiO<sub>2</sub>-EC catalyst could be easily recycled by filtration after each reaction run with negligible Au leaching as confirmed by ICP analysis. Consequently, it exhibits stable catalytic performances during continuous reaction cycles. For example, after 9 recycles, it still gives the conversion of 3-nitrostyrene higher than 97.0% and selectivity of 3-aminostyrene higher than 99.0% (Figure 6A). Very importantly, it is worth noting that the reaction rate of 3-nitrostyrene at the beginning of each run is very similar, indicating the good stability of the Au/TiO<sub>2</sub>-EC catalyst (Figure 6B).

**3.6 Large-scale reaction.** When the amount of 3nitrostyrene in the hydrogenation is a 4.8-g scale, the Au/TiO<sub>2</sub>-EC still gives the conversion at 96.7% and 3aminostyrene selectivity at 99.0% (Scheme S2). In this case, the turnover frequency (TOF) of the Au/TiO<sub>2</sub>-EC could reach to 279 h<sup>-1</sup> calculated from the total amount of Au in the reaction system. This TOF value (279 h<sup>-1</sup>),

Catalyst	$TOF(h^{-1})^{b}$				
	Nitrobenzene	Styrene	Acetophenone	Chlorobenzene	
Au/TiO <sub>2</sub> -EC	545	150	154	<10	
Au/TiO <sub>2</sub> -Con	375	168	177	<10	
Au/TiO <sub>2</sub> -EC <sup>c</sup>	469	d	d	<sup>d</sup>	
Au/TiO <sub>2</sub> -Con <sup>c</sup>	298	34	21	<sup>d</sup>	

Table 2. TOFs of the Au/TiO<sub>2</sub>-EC and Au/TiO<sub>2</sub>-Con in the hydrogenation of various substrates.<sup>a</sup>

<sup>a</sup> Reaction conditions: 0.3 mmol of substrate, 10 bar of H<sub>2</sub>, 5 mg of catalyst, and 3 ml of toluene; <sup>b</sup> Calculated from all the Au atoms in the reaction system; <sup>c</sup> A mixture of nitrobenzene (0.3 mmol), styrene (0.3 mmol), acetophenone (0.3 mmol), and chlorobenzene (0.3 mmol) were employed as substrates; <sup>d</sup> Undetectable.

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which even obtained under relatively mild reaction conditions, is still much higher than that (<173 h<sup>-1</sup>) of the conventional Au nanocatalysts.<sup>35</sup> Furthermore, systematic investigations were carried out by employing various substrates (Table S1 and S2), showing that the Au/TiO<sub>2</sub>-EC catalyst is generally active for chemoselective hydrogenation of different substituted nitroarenes (Table S1). The excellent catalytic activity and selectivity combined with the generalized applicability make the Au/TiO<sub>2</sub>-EC catalyst potentially useful for wide applications for chemoselective hydrogenation of substituted nitroarenes.



**Figure 6.** Recycling tests of selective hydrogenation of 3nitrostyrene over the Au/TiO<sub>2</sub>-EC catalyst. The reaction conditions are the same to those described in Table 1. (A) Conversion of 3-nitrostyrene and selectivity to 3aminostyrene in each run; (B) Conversion of 3-nitrostyrene at the beginning (30 min) of each run. The black straight lines are made by fitting the conversion points. Clearly, these straight lines have similar slopes, suggesting similar conversion rate in each run.

#### 4. CONCLUSIONS

In summary, we have reported Au nanoparticles supported on the edge/corner sites of anatase are highly active and selective for the hydrogenation of substituted nitroarenes. When 3-nitrostyrene is used as reactant in the hydrogenation, the Au/TiO<sub>2</sub>-EC catalyst gives TOF as high as 279 h<sup>-1</sup> with 3-aminostyrene selectivity higher than 99.0%, which are the best results achieved over Au nanocatalysts yet. The superior properties of the Au/TiO<sub>2</sub>-EC can be attributed to the unique adsorption and activation of nitro-groups compared to the conventional Au/TiO<sub>2</sub>, leading to simultaneous enhancement in catalytic activity and chemoselectivity. The approach in this work can be potentially used to develop novel efficient catalysts for chemoselective hydrogenations in the future.

#### ASSOCIATED CONTENT

**Supporting Information**. The XPS, IR, DFT and detailed catalytic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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#### REFERENCES

(1) Xu, Z., Xiao, F.-S., Purnell, S. K., Alexeev, O., Kawi, S., Deutsch, S. E., Gates, B. C. *Nature* **1994**, *372*, 346-348.

(2) Corma, A., Serna, P. Science 2006, 313, 332-334.

(3) Schlögl, R. Angew. Chem. Int. Ed. 2015, 54, 3465-3520.

(4) Liu, X., Li, H., Ye, S., Liu, Y.-M., He, H.-Y., Cao, Y. Angew. Chem. Int. Ed. **2014**, *53*, 7624-7628.

(5) He, D., Jiao, X., Jiang, P., Wang, J., Xu, B.-Q. Green Chem. 2012, 14, 111-116.

(6) Lu, J., Serna, P., Aydin, C., Browning, N. D., Bates, B. C. J. Am. Chem. Soc. **2011**, *133*, 16186-16195.

(7) Korstanje, T. J., van der Vlugt, J. I., Elsevier, C. J., de Bruin, B. *Science* **2015**, *350*, 298-302.

(8) Sun, K.-Q., Hong, Y.-C., Zhang, G.-R., Xu, B.-Q. ACS Catal. 2011, 1, 1336-1346.

(9) Kyriakou, G., Boucher, M. B., Jewell, A. D., Lewis, E. A., Lawton, T. J., Baber, A. E., Tierney, H. L., Flytzani-Stephanopoulos, M., Sykes, E. C. H. *Science* **2012**, *335*, 1209-1212.

(10) Cisneros, L., Serna, P., Corma, Angew. Chem. Int. Ed. **2014**, *53*, 9306-9310.

(11) Luo, W., Sankar, M., Beale, A. M., He, Q., Kiely, C. J., Bruijnincs, P. C. A., Weckhuysen, B. M. *Nat. Commun.* **2014**, *6*, 6540.

(12) Schwab, F., Lucas, M., Claus, P. Angew. Chem. Int. Ed. **2011**, *50*, 10453-10456.

(13) Takato, M., Takahashi, Y., Ichikawa, S., Mizugaki, T., Jitsukawa, K., Kaneda, K. *Angew. Chem. Int. Ed.* **2013**, *52*, 1481-1485.

(14) Lucci, F. R., Liu, J. L., Marcinkowski, M. D., Yang, M., Allard, L. F., Flytzani-Stephanopoulos, M.,Sykes, E. C. H. *Nat. Commun.* **2015**, *6*, 8550.

(15) Yardimci, D., Serna, P., Gates, B. C. ACS Catal. 2012, 2, 2100-2113.

(16) Sergeev, A. G., Hartwig, J. F. Selective, *Science* **2011**, *332*, 439-443.

(17) Liu, H. Z., Jiang, T., Han, B. X., Liang, S. G., Zhou, Y. X. Science **2009**, *326*, 1250-1252.

(18) Ma, Z., Dai, S. ACS Catal. 2011, 1, 805-818.

(19) Teschner, D., Borsodi, J., Wootsch, A., Revay, Z., Haevecker, M., Knop-Gericke, A., Jackson, S. D., Schloegl, R. *Science* **2008**, *320*, 86-89.

(20) Wang, G.-H., Hilgert, J., Richter, F. H., Wang, F., Bongard, H. J., Spliethoff, B., Weidenthaler, C., Schuth, F. Nat. Mater. 2014, 13, 294-301. (21) C. W. A Chan, A. H. Mahadi, M. M.-J. Li, E. C. Corbos, C. Tang, G. Jones, W. C. H. Kuo, J. Cookson, C. M. Brown, P. T. Bishop, S. C. E. Tsang, Nat. Commun. 2014, 5, 5787. (22) Schrader, I., Warneke, J., Backenkohler, J., Kunz, S. J. Am. Chem. Soc. 2015, 137, 905-912. (23) Korirala, S., Scholfie, C. R., Selke, E, Doutton, H. J. J. Am. Chem. Soc. 1973, 50, 11-15. (24) Kahsar, K. R., Schwartz, D. K., Medlin, J. W. J. Am. Chem. Soc. 2014, 136, 520-526. (25) Pang, S. H., Schoenbaum, C. A., Schwartz, D. K., Medlin, J. W. Nat. Commun. 2013, 4, 2448. (26) Davis, S., Zeara, F., Somorjai, G. J. Catal. 1984, 85, 206-223. (27) Lee, H., Habas, S., Somorjai, G., Yang, P. J. Am. Chem. Soc. 2008, 130, 5406-5407. (28) Lee, I., Delbecq, F., Morales, R., Albiter, M., Zaera, Nat. Mater. 2009, 8, 132-138. (29) Niu, W., Gao, Y., Zhang, W., Lu, X. Angew. Chem. Int.

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- Ed. 2015, 54, 8271-8274.
- (30) Zhang, H., Gu, X.-K., Canlas, C., Kropf, A. J., Aich, P.,
- Greeley, J. P., Elam, J. W., Meyers, R. J., Dumesic, J. A., Stair, P. C., Marshall, C. L. Angew. Chem. Int. Ed. 2014, 53, 12132-
- 12136. (31) Wei, H., Liu, X., Wang, A., Zhang, L., Qiao, B., Yang, X.,
- Huang, Y., Miao, S., Liu, J., Zhang, T. Nat. Commun.2014, 5, 5634
- (32) Mitsudome, T., Mikami, Y., Matoba, M., Mizugaki, T., Jitsukawa, K., Kaneda, K. Angew. Chem. Int. Ed. 2012, 51, 136-139
- (33) Jagadeesh, R. V., Surkus, A.-E., Junge, H., Pohl, M.-M., Radnik, J., Rabeah, J., Huan, H. M., Schunemann, V., Bruckner, A., Beller, M. Science 2013, 342, 1073-1076.
- (34) Westerhaus, F. A., Jagadeesh, R. V., Wienhoefer, G., Pohl, M. M., Radnik, J., Surkus, A.-E., Rabeah, J., Junge, K., Junge, H., Nielsen, M., Brueckner, A., Beller, M. Nat. Chem. **2013**, *5*, 537-543.
- (35) Serna, P., Concepcion, P., Corma, A. J. Catal.2009, 265, 19-25.
- (36) Boronat, M., Concepcion, P., Corma, A., Gonzalez, S., Illas, F., Serna, P. J. Am. Chem. Soc. 2007, 129, 16230-16237.
- (37) Yang, H., Cui, X, Dai, X., Deng, Y., Shi, F. Nat. Commun. **2015**, 6, 6478.
- (38) Boronat, M., Concepción, P., Corma, A., González, S., Illas, F., Serna, P. J. Am. Chem. Soc. 2007, 129, 16230-16237.
- (39) Chen, M. S., Goodman, D. W. Science 2004, 306, 252-255.
- (40) Valden, M., Lai, X., Goodman, D. W. Science 1998, 281, 1647-1650.
- (41) Enache, D. I., Edwards, J. K., Landon, P., Solsona-Espriu, B., Carley, A. F., Herzing, A. A., Watanabe, M., Kiely, C. J.,
- Knight, D. W., Hutchings, G. J. Science 2006, 311, 362-365. (42) Matthey, D., Wang, J. G., Wendt, S., Matthiesen, J.,
- Schaub, R., Laegsgaard, E., Hammer, B., Besenbacher, F. Science 2007, 315, 1692-1696.
- (43) Saavedra, J., Doan, H. A., Pursell, C. J., Grabow, L. C., Chandler, B. D. Science 2014, 345, 1599-1602.
- (44) Wang, L., Wang, H., Rice, A. E., Zhang, W., Li, X., Chen, M., Meng, X., Lewis, J. P., Xiao, F.-S. J. Phys. Chem. Lett. 2015, 6,2345-2349.
- (45) Shiraishi, Y., Hirakawa, H., Togawa, Y., Sugano, Y., Ichikawa, S., Hirai, T. ACS Catal. 2013, 3, 2318-2326.
- (46) Parr, R. G., Yang, W. J. Am. Chem. Soc. 1984, 106, 4049-4050.
- (47) Yang, W., Parr, R. G. Proc. Natl. Acad. Sci. U. S. A.1985, 82, 6723-6726.
- (48) Kinomoto, Y., Watanabe, S., Takahashi, M. & Ito, M. Surf. Sci. 1991, 242, 538-543.
- (49) Liu, X., Wang, A., Li, L., Zhang, T., Mou, C.-Y., Lee, J.-F. *J. Catal.* **2011**, *278*, 288-296

