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# Rational Control on the Selectivity of Ru Catalyst for Hydrogenation of 4-Nitrostyrene via Strain Regulation

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Abstract: Tuning the selectivity of metal catalysts is of paramount importance, yet a great challenge. Here, a new strategy to effectively control the selectivity of metal catalysts, by tuning the lattice strain, is reported. In this approach, we introduce a certain amount of Co atoms into Ru catalysts to compress the Ru lattice, as confirmed by aberration corrected high-resolution transmission electron microscopy (HRTEM) and X-ray absorption fine structure (XAFS) measurements. We discover that, the lattice strain of Ru catalysts can greatly affect their selectivity and Ru with 3% lattice compression exhibits extremely high catalytic selectivity for hydrogenation of 4-nitrostyrene to 4-aminostyrene compared to pristine Ru (99% Vs. 66%). The theoretical studies prove that the optimized lateral compressive strain facilitates hydrogenation of nitro-group but impedes the hydrogenation of vinyl-group. This study provides a new guideline for designing metal catalysts with high selectivity.

Tuning the selectivity of metal catalysts is highly desirable due to their significance for the development of energy-saving chemical processes. Generally, a molecule with one functional group can be converted into a desired product using a certain metal catalyst. But it's very challenging to selectively handle just a specific functional group when other competing functional groups exist in the same molecule.<sup>[1]</sup> For instance, selective reduction of nitro-group in the presence of vinyl-group is a crucial step to obtain functionalized anilines.<sup>[2]</sup> However, the conventional Pt, Pd and Ru catalysts can simultaneously reduce the nitro- and vinyl- groups, leading to undesired byproducts. Thus, there is a strong incentive to develop effective strategies for improving the selectivity of metal catalysts.

The compressed or expanded arrangements of surface atoms will alter the crystal lattice strain. Recent reports demonstrated that the catalytic activity could be influenced by tuning the lattice strain of metal catalysts because the lattice strain can modify the electronic structure of catalysts and further affect the adsorption of reactants.<sup>[3]</sup> Take oxygen reduction reaction (ORR) as an example, lattice strain can tune the ORR activity by modifying the bind energy of intermediate oxygenated

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species and, thereby, changes the activation barriers for protonand electron-transfer processes.<sup>[4]</sup> In this regard, tuning the lattice strain of metal catalysts might be a new effective strategy to control their catalytic selectivity.



Figure 1. Representative (a) TEM, (b) STEM image and (c) EDS elemental mappings of Co-Ru NPs. (d) Atomic-resolution HAADF-STEM images of Co-Ru NPs. (e)  $\epsilon xx$  strain component determined via geometric phase analysis.

In this study, we discover that the selectivity of Ru catalysts can be rationally controlled by compressing Ru lattice strain. The lattice compression of Ru is achieved via preparing a novel dumbbell-shaped Co-Ru nanostructure composed of a Co nanorod with two ends capped with Ru nanoplates. The crystal lattice of Ru at both ends is compressed due to the connection of Co at the center compared to pristine Ru, as confirmed by aberration corrected HRTEM and XAFS studies. The hydrogenation of 4-nitrostyrene demonstrates that, Ru with 3% lattice compression can achieve nearly total conversion of 4-nitrostyrene to 4-aminostyrene, which is superior to pristine Ru. Density functional theory (DFT) calculations reveal that the optimized lateral compressive strain facilitates hydrogenation of PhNO<sub>2</sub> but impedes the hydrogenation of C<sub>2</sub>H<sub>4</sub>, which help to understand the strain effects of metal catalysts.

As shown by transmission electron microscopy (TEM, Figure 1a) and scanning electron microscopy (SEM, Figure S1 in the Supporting Information), the as-obtained products have uniform dumbbell-shaped nanostructures consisting of one nanorod and two nanoplates grown on its ends respectively. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image (Figure 1b) and the corresponding energy-dispersive x-ray (EDX) elemental mapping (Figure 1c)

show that the prepared nanoparticles (NPs) are composed of core rich in Co atoms and shell rich in Ru atoms. We utilized aberration-corrected HAADF-STEM (Figure 1d and Figure S2) to investigate the compressive lattice strain of Ru induced by effect of Co. As shown in Figure 1d, the measured lattice fringe on both ends (Ru) is 2.08 Å which is smaller than that of pristine Ru (0001) (2.14Å), representing ~3% compressive strain. In order to study the effect of Co atoms on the compressive strain of Ru, we conducted the geometric phase analysis (GPA) and the ɛxx component of the strain tensor is shown in Figure 1e (the  $\varepsilon_{yy}$ component and diffractogram are shown in Figure S3 and Figure S4, respectively). It illustrates that the inner part of the nanoparticle is more compressive than the outer part, which demonstrates that the introduction of Co atoms into Ru nanostructures resulted in smaller lattice distance of Ru, i.e. the compressive stress. X-ray diffraction (XRD) analysis was conducted to characterize the crystallinity of the Co-Ru NPs (Figure S5). The broadened (0001) and (10-11) peaks together with (10-10) peak can be assigned to the hexagonal closepacked (hcp) structure of Ru, and no obvious Co diffraction peaks can be found. The composition of the prepared NPs was analyzed using EDX and inductively coupled plasma-mass spectrometry (ICP-MS). The Co/Ru atomic ratio determined by EDX analysis was 0.23/0.77 (Figure S6), which was coincide with ICP-MS results. Co-Ru NPs with different Co/Ru ratios were easily achieved by varying the feeding ratio of Co(acac)<sub>2</sub>/Ru<sub>3</sub>(CO)<sub>12</sub> and analyzed by TEM (Figure S7) and EDX (Figure S8-S10). As shown in Figure S11, there is a linear correlation between the synthetic feeding ratio of Co/Ru and analyzed molar ratio. We also monitored the reaction process of the Co-Ru NPs (Figure S12). First, the samples were obtained along the "axial growth" mode at the initial stage of NPs formation. As the reaction continues, the growth mode of samples changed from "axial growth" mode to "radial growth" mode. When the reaction was extended to 2.0 h, the stable phase Co-Ru NPs were formed, and the "radial growth" finished.

We used X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) to further investigate the local atomic and electronic structures of the Co-Ru NPs. Figure 2a shows the XANES curves of Ru K-edge. It is found that the Ru K-edge of the samples is close to that of Ru foil reference, suggesting that the oxidation state of Ru in the samples should be zero. The slightly lower intensity of Ru Kedge XANES oscillation of the samples may be due to the size effect and heteroatomic interaction in binary NPs.<sup>[5]</sup> From the XANES spectra of Co K-edge in Figure 2b, we can find that the intensity of the white line peaks (the peak A) of the samples is stronger than that of Co foil and the absorption threshold (shown in the dashed frame) shifts to higher energy, indicating the variation of the Co 3d-band electron density.<sup>[6]</sup> Interestingly, the position of the peak B is regularly changed with the Co content. The above phenomena indicated that the Co core interacts with the Ru shell. In order to further investigate the interaction between Ru and Co, Fourier transform (FT) EXAFS (without phase correction) analysis is performed at Ru K-edge (Figure 2c) and Co K-edge (Figure 2d). In FT-EXAFS spectra of Ru Kedge, there is a strong peak located at 2.0 to 2.6 Å and it is related to Ru-Ru single scattering. Locally amplified graph (the

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insert in Figure 2c) shows that a shoulder peak exists at about 2.1 Å, and its intensity seen to be stronger and stronger with the variation of Ru content. Here, we suppose that the shoulder peak is due to Ru-Co scattering. Similar case can be seen in FT-EXAFS curves of Co K-edge (Figure 2d). The main peak at about 2.2 Å is due to Co-Co single scattering and the shoulder peak at about 2.5 Å results from Co-Ru interaction. The above results revealed that there is a strong interaction between Co core and Ru shell, and Ru-Ru bond gradually shrinks with increasing the Co component in Co-Ru NPs. Additional information of Ru K-edge and Co K-edge is provided in the Supplementary Information (Figure S13-S17, Table S1-S2).



Figure 2. XANES spectra of Co-Ru NPs for (a) Ru K-edge and (b) Co K-edge. EXAFS spectra for (c) Ru K-edge and (d) Co K-edge.

As is well-known, Ru-based NPs have been widely used in many catalytic reactions.<sup>[7]</sup> As a proof-of-concept application, the Co-Ru NPs with different compressive strain were used in hydrogenation of 4-nitrostyrene to study the relationship between lattice strain and catalytic selectivity. The introduction of Co atoms into Ru NPs would slightly decrease the reaction rate. All the catalysts could achieve complete conversion after 12 hours. Figure 3a shows three typical products for 4nitrostyrene (a) hydrogenation in a reaction scheme. The hydrogenation reaction proceeds through two routes, i.e., selective reduction of nitro-group giving target product 4aminostyrene (b), or preferential attack of the C=C functionality producing undesired by-product 4-nitroethylbenzene (c). Then, fully hydrogenated byproduct 4-ethylbenzenamine (d) would be produced through above two routes. The selectivity of b and c when reached complete conversion were showed in Figure 3b as contrast. We found that Ru and Co<sub>0.46</sub>-Ru<sub>0.54</sub> NPs produced comparable 4-nitroethylbenzene (c) to 4-aminostyrene (b); Co<sub>0.12</sub>-Ru<sub>0.88</sub> and Co<sub>0.38</sub>-Ru<sub>0.62</sub> gave relative lower selectivity of c. Notably, almost no 4-nitroethylbenzene was found using Co<sub>0.23</sub>-Ru<sub>0.77</sub> as a catalyst, indicating its specific hydrogenation

selectivity on nitro-group. Interestingly, the selectivity of b is in a volcano-type fashion with increasing the compressive lattice strain of Ru. Pristine Ru gave only 66% selectivity of b, and the selectivity was increased to 99% when compressing the Ru lattice strain with 3%; however, decreased selectivity was found when further increasing the compressive lattice strain gradually. The above data collectively demonstrated that Ru with 3% compressive strain could realize highly selective performance in catalytic hydrogenation of 4-nitrostyrene to 4-aminostyrene. Moreover, the Co<sub>0.23</sub>-Ru<sub>0.77</sub> catalysts could be easily recycled for at least 4 times without any obvious loss of activity and selectivity, demonstrating the high stability of the catalysts.



**Figure 3.** (a) Reaction network of the hydrogenation of 4-nitrostyrene, (b) The selectivity of 4-aminostyrene and 4-nitroethylbenzene using Co-Ru catalysts with different compressive lattice strain, and (c) Recycle test of the  $Co_{0.23}$ -Ru<sub>0.77</sub> catalysts in the hydrogenation of 4-nitrostyrene.

DFT calculations were carried out to verify whether the selectivity of catalyst is determined by the lattice strain of Ru. Two prototypes,  $C_2H_4@Ru(0001)$  and  $PhNO_2@Ru(0001)$ , were chosen to investigate the catalysis selectivity. For  $C_2H_4@Ru$  (0001), one carbon atom was located at the Ru top site, and the other one was located at the hollow site, which is consistent with the early study. <sup>[8]</sup> The full reaction pathways for ethylene

hydrogenation are investigated according to the Horuit-Polanyi mechanism<sup>[9]</sup> with two elementary steps  $C_2H_4^* + H^* \rightarrow C_2H_5^*$  and  $C_2H_5^* + H^* \rightarrow C_2H_6^*$ . The reaction pathways are shown in Figure 4a. Ethylene adopts the  $\pi$  adsorption mode when hydrogen atom covers on the surface, which is consistent with Christopher's study.<sup>[10]</sup> The first hydrogen addition step is endothermic, while the second hydrogen addition step is exothermic by 10.41 kcal/mol. The activation barriers for the first and second steps are 29.25 and 12.64 kcal/mol, indicating that the first hydrogenation process is the rate-limiting step. When the lateral strains were applied, the full reaction pathways changed significantly. Under 3% lateral compressive strain, the first activation barrier increases slightly, while the second barrier increases significantly compared with the lateral strain free system, making the second step as the rate-limiting step. By increasing the lateral compressive strain to 6%, the first activation barrier decreases to 17.25 kcal/mol, which facilitates the hydrogenation from ethylene to ethyl.

For PhNO<sub>2</sub>@Ru (0001), previous studies have indicated that the parallel adsorption mode over the metal surface is preferable over vertical adsorption mode. Meanwhile, the direct reaction pathway is preferable over indirect reaction pathway.<sup>[11]</sup> Hence, in this study, only the parallel adsorption mode together with direct reaction pathway are considered. Because identifying all transition-state structures along the potential energy surface is computationally prohibitive for this system, we optimized the geometries of key intermediates in the direct pathways to compare the stability of the intermediates based on the scheme provided by Mahata et al.[12] In parallel adsorption mode, nitrobenzene was placed parallel to the Ru (0001) surface, where the  $\pi\text{-electron}$  of the aromatic ring is in direct interaction with metal surface. PhNO<sub>2</sub> is first reduced to nitrosobenzene (PhNO), which is accompanied by energy release (20.61 Kcal/mol, Fig 4b.) Hydrogen atom can attack PhNO intermediate either on O-atom or N-atom which subsequently forms PhNOH and PhNHO intermediates respectively. These two steps are calculated to be endothermic by 10.75 and 5.27 Kcal/mol, respectively. In the next step, one hydrogen atom interacts with either PhNOH or PhNHO intermediate to form PhNHON intermediate. These two steps are calculated to be endothermic by 9.37 and 14.85 Kcal/mol, respectively. As PhNHOH is a very stable intermediate,<sup>[13]</sup> the formation of PhNHOH should not proceed through high endothermic pathway (via PhNHO intermediate). The formed PhNHOH react with one hydrogen atom to form the PhNH intermediate. The high exothermic value (-38.30 Kcal/mol) was due to the N-O bond breaking. Generally, the reaction steps of nitrobenzene to aniline are exothermic. When the lateral strains were applied, the energy profiles changed significantly. When a 3% lateral compressive strain was applied on the surface, all the relative energies of intermediates changed slightly expect for PhNHOH. Exothermic value for step PhNOH→PhNHOH changed from -9.37 to -5.92 Kcal/mol, which facilitates the reaction. However, under an even larger lateral compressive strain, say 6%, the reduction reaction may be blocked. Firstly, a huge endothermic value is needed in the formation of PhNOOH. Secondly, the PhNOH is highly unstable in this condition, which would make the PhNHO  $\rightarrow$ PhNHOH step as the preferable step. Overall, a 3% lateral

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compressive strain can facilitate the reaction. When a larger lateral compressive strain (6%) is applied, the entire reaction may be blocked. Based on the above results of both  $C_2H_4@Ru(0001)$  and  $PhNO_2@Ru(0001)$ , we determined that the small lateral compressive strain facilitates hydrogenation of PhNO2 but impedes the hydrogenation of  $C_2H_4$ . With increasing lateral strain, the hydrogenation of  $PhNO_2$  is impedes but the hydrogenation of  $C_2H_4$  process is facilitated.



Figure 4. (a) Reaction pathways for the hydrogenation of  $C_2H_4$  over Ru (0001) surface (b) Relative energy profile for the reduction reaction from PhNO<sub>2</sub> to PhNH<sub>2</sub>.

In summary, we have demonstrated that the selectivity of metal catalysts could be effectively controlled by rationally tuning metal lattice strain. The aberration corrected HRTEM and XAFS studies proved that introducing Co atoms into Ru catalysts could compress the Ru lattice strain. We observed obvious improvement (from 66% to 99%) in Ru catalytic selectivity for hydrogenation of 4-nitrostyrene to 4-aminostyrene under 3% lattice compression, which is consistent with the theoretical calcination results. We believe that such an approach could help us to achieve the rational design of ideal metal catalysts, which have wide applications beyond hydrogenation reaction.

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**Keywords:** Ru nanoparticle • metal catalysts • lattice strain • hydrogenation reaction

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