Fabrication and engineering of Ru local structures toward enhanced kinetics of hydrogen generation

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Abstract

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Abstract A strategy to boost hydrogen generation from ammonia borane hydrolysis was proposed by engineering Ru local structures via the employment of Cl-free Ru precursors and acid-leaching of the bimetallic Ru-Co catalysts. The effects of Cl and Co were separately investigated by comparing the Cl-free/Clcontaining monometallic Ru catalysts and Co-leaching/Co-containing bimetallic Ru-Co catalysts, respectively. Decoupled from the Co electronic effects (electron transfer from Co to Ru), the Cl geometric effects (site blockage and steric hindrance) were identified as the main factors, which could be further promoted by introducing more low-coordinated Ru sites. The increase of Co content gives rise to more edge-like Ru active sites after acid leaching, with a lower H_2O activation barrier for hydrogen production. Consequently, al-Ru₁Co with the most edge-like Ru active sites demonstrated a 4.1-fold increase in catalytic activity. The insights revealed here might guide the design and preparation of metal catalysts with the maximum active sites.

Keywords: local structure; hydrogen generation; active sites; geometric and electronic effects; acid leaching.

Introduction

Hydrogen appears to be one of the most promising and renewable energy sources to the energy and environmental crises, while the efficient and safe hydrogen storage and production are the main technological obstacles in establishing a hydrogen-powered society¹⁻⁵. Ammonia borane (NH₃BH₃, AB), owing to its high hydrogen content (19.6 wt%), long-term stability and nontoxicity at room temperature, has been regarded as a potential hydrogen storage material⁶⁻⁹. Typically, the hydrogen stored in ammonia borane can be released by either pyrolysis or hydrolysis¹⁰⁻¹². Although pyrolysis enables the regeneration of ammonia borane after usage, it is plagued by the requirement for high temperatures and the sluggish kinetics of hydrogen production¹³⁻¹⁵. By contrast, hydrolysis provides a fast hydrogen generation rate at mild conditions under proper catalysts, rendering it more appealing for practical application¹⁶⁻¹⁸. Hence, continuous efforts have been devoted to design and fabricate highly efficient catalysts to improve hydrolysis efficiency.

Various types of catalysts, including noble metals (e.g., Ru, Pt, Rh, Pd and Au) and nonnoble metals (Fe, Co, Ni and Cu), have been evaluated for the hydrolysis of ammonia borane, among which Ru- and Pt-based catalysts show the highest catalytic activity¹⁹⁻²³. Considering their limited abundance and high cost, it still remains challenging yet highly desirable to further improve their catalytic activity and minimize their usage. Exemplified by Ru catalysts, strategies have been proposed to tune the electronic properties of active site and the resultant catalytic activity by: (i) introducing multi-metallic components with different structures^{24,25}, such as alloys and core-shells, (ii) creating Ru–ligand interfacial bonding interactions based on the electron-withdrawing/donating properties^{26,27}, (iii) constructing Ru–support interactions by varying the identity and properties of the support^{28,29}, and (iv) taking the advantage of confinement within porous organic cages and zeolites^{30,31}. As a result, significant improvements in the active site reactivity, that is, turnover frequency (TOF), have been recently achieved for this reaction.

As known, metal catalyst surfaces typically compose of abundant active sites working together as an ensemble for chemicals conversion, which the resultant catalytic performance is determined by both the quality (TOF) and quantity (N) of active site, i.e., $r=TOF \times N$. Based on this, apart from the above strategies to increase the TOF, the catalytic activity can be further improved by maximizing the quantity of active sites, N. However, it is worth to note that the traditional downsizing metal particles methods are not usually effective because not all of the surface atoms are active^{32,33}. Hence, the identification of Ru active sites has emerged as a prerequisite for increasing the quantity of Ru active sites, which enables synergy between the quality and quantity of Ru active sites for this reaction. In our recent work, the Ru edge site has been identified as the main active site based on morphology characterization, particle modeling and kinetic analysis, providing a good opportunity for designing highly efficient Ru catalysts³⁴. However, to the best of our knowledge, few studies have been conducted on tuning the quantity of Ru active site for ammonia borane hydrolysis, possibly due to the lack of knowledge about Ru active site. In this regard, it is highly desirable to gain a fundamental understanding of the Ru active site in terms of its local and electronic structure to fine-tune the quantity and quality of Ru active sites to promote hydrogen production.

In this work, we report a strategy to boost the quantity and quality of Ru active sites by employing a Cl-free Ru precursor and the acid leaching of bimetallic Ru-Co catalysts, giving rise to a 4.1-fold increment in hydrogen generation rate from ammonia borane. Excluding the size effect, a series of Cl-free bimetallic RuCo/CNT catalysts with different Co loadings were prepared and tested for this reaction and were compared with the Cl-containing monometallic Ru_{Cl}/CNT catalyst. The effects of Cl and Co on the Ru local structure were separately investigated by further comparing Cl-free/Cl-containing monometallic Ru catalysts and Co-leaching/Co-containing bimetallic Ru-Co catalysts, respectively, based on the combination of multiple characterization techniques, kinetic (isotopic) analyses, and DFT calculations. Decoupled from the electronic effects (electron transfer), the geometric effects (site blockage and steric hindrance) of Ru were identified as

the primary factors promoted by acid leaching to introduce more low-coordinated Ru active sites.

2. Experimental

2.1. Catalyst preparation and testing

Pristine multi-walled carbon nanotubes (CNT, purchased from Beijing Cnano Technology Limited) were employed as support to prepare the Ru and/or Co catalysts. Typically, a certain amount of CNT was mixed with an aqueous solution of Ru(NO)(NO₃)₃(ruthenium(III) nitrosyl nitrate, Alfa Aesar) and/or Co(NO)₃·6H₂O (Sinopharm Chemical Reagent Co. Ltd). The Ru loading was kept at 1.5 wt% for all the catalysts, and the molar ratio of Ru to Co was set as 3:1, 2:1 and 1:1. The as-prepared samples were placed at room temperature and then at 80 °C under stagnant air for 12 h. Next, the catalyst precursors were reduced by pure H₂ at 250 °C for 2 h, followed by cooling to room temperature under Ar. To inhibit bulk oxidation, the as-obtained catalysts were further passivated by 1% O₂/Ar for another 20 min. The catalysts were denoted as Ru₃Co/CNT, Ru₂Co/CNT and Ru₁Co/CNT. Acid leaching was conducted by mixing the bimetallic RuCo/CNT catalysts (0.5 g) with 50 mL of dilute HNO₃ (0.01 M) for 20 min at room temperature. The as-obtained catalysts were filtered, washed and dried at 80 °C for 12 h, and denoted as al-Ru₃Co/CNT, al-Ru₂Co/CNT and al-Ru₁Co/CNT.

2.2. Catalytic testing

The catalytic testing of these catalysts for ammonia borane hydrolysis was performed in a three-neck flask containing a magnetic stirrer. The flask was immersed in a water bath to control the reaction temperature at 25 °C. Prior to the reaction, 0.05 g of catalyst was transferred into the flask, and the reaction was initiated by injecting an aqueous ammonia borane solution (5 mL, 0.01 g[?]mL⁻¹) into the flask with a stirring speed of 900 rpm. A glass gas burette filled with H2O was connected to the reaction flask to record the amount of discharged H2O, which was weighed by an electronic balance and converted into the volume of evolved hydrogen. These catalysts were also used for ammonia borane hydrolysis at elevated temperatures (30, 35 and 40 degC) to obtain the activation energy and pre-exponential factor. The kinetic isotopic experiments were performed by replacing H_2O with D_2O as the reactant under the same reaction conditions.

2.3. Characterization

The metal particle size distributions of the catalysts were determined by high-angle annular dark fieldscanning transmission electron microscopy (HAADF-STEM) on a Tecnai G2 F20 S-Twin microscopy. The catalyst morphologies were characterized by high-resolution transmission electron microscopy on a JEOL JSM-2100 electron microscopy operating at 200 kV. The electronic properties were characterized by X-ray photoelectron spectrometry (XPS) on a ThermoFisher ESCALAB250Xi equipped with an Al K_{α} X-ray (1486.6 eV, excitation source working at 15 kV); the C *1s* peak at 284.6 eV was used to calibrate the binding energy. The contents of Ru and Co within the spent acid solution were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on an Agilent 725-ES. H₂-temperature-programmed reduction (H₂-TPR) measurements were conducted on a Micrometrics Autochem 2920 chemisorption instrument equipped with a thermal conductivity detector.

2.4. DFT calculation

The DFT calculations were performed by VASP³⁵⁻³⁸ with the projected augmented wave (PAW) method³⁹, and the exchange-correlation functional was generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) method⁴⁰. The Kohn-Sham orbitals were expanded in a plane-wave basis set with a kinetic cutoff energy of 450 eV⁴¹. The sampling of the Brillouin zone was performed using a Monkhorst-Pack scheme. The equilibrium lattice constant of a = 2.72 Å and c = 4.31 Å are obtained for bulk Ru in the hcp structure, which agrees well with the experimental bulk lattice constant (a=2.71 Å and c=4.28 Å). The surface slabs of Ru(001), Ru(101) and Ru(111) were respectively modeled with $p(4 \times 4)$, $p(2 \times 4)$ and $p(2 \times 2)$ supercells with a vacuum region of 15 Å, where the bottom two-layer Ru atoms were fixed and the top two-layer Ru atoms were relaxed. For all the calculations, the geometry optimization was converged until the forces on each atom were less than 0.03 eV/Å and the total energy differences were less than 10⁻⁵ eV. The H₂O activation energy was calculated as $\Delta E_a = E_{TS} - E_{ads}$, where the E_{TS} is the energy of transition state (TS), the E_{ads} is the adsorption energy of H₂O. The H₂O adsorption energy was calculated as $E_{ads} = E_{H2O/surface} - E_{H2O} - E_{surface}$, where $E_{H2O/surface}$ is the total energy of the surface adsorbed with H₂O, $E_{surface}$ is the total energy of the clean surface, and E_{H2O} is the total energy of isolated H₂O. The Bader analysis was implemented with a fast algorithm, and the core charge density was included in the partitioning. The charge density difference images were obtained by VESTA visualization software.

3. Results and discussion

3.1. Significantly improved hydrogen generation kinetics

In light of the catalytic performance mainly determined by the metal local environment, both Ru(NO)(NO₃)₃ and Co(NO)₃·6H₂O were used to prepare Cl-free bimetallic Ru-Co catalysts with different Ru/Co ratios, i.e., Ru₃Co/CNT, Ru₂Co/CNT and Ru₁Co/CNT, with the aim of significantly altering the local structure of Ru atoms for this reaction. Considering that Ru-catalyzed ammonia borane hydrolysis has been suggested as a highly structure-sensitive reaction³⁴, the particle sizes of these catalysts were first evaluated, prior to the catalytic testing. High-resolution HAADF-STEM was employed to characterize the particle size distribution of the catalysts. As shown in Figure S1, all three catalysts exhibited a relatively homogenous distribution of metal particles over the CNT surface. Based on the measurements of more than 200 random particles, the average metal particle sizes were determined to be 1.34 ± 0.36 , 1.33 ± 0.35 , and 1.40 ± 0.37 nm for Ru₃Co/CNT, Ru₂Co/CNT, and Ru₁Co/CNT, respectively. The metal particle size remained almost unchanged despite of the addition of Co to Ru. This indicates that Ru can promote the distribution of Co and obtain the similar-sized metal catalysts, which would help to minimize the effect of particle size and enable a fair comparison of the Ru local structure for this reaction.

With similar metal particle sizes, these three catalysts were tested for the hydrolytic dehydrogenation of ammonia borane under the same reaction conditions, and the results are shown in Figure S2. In the initial stage of reaction, all three catalysts exhibited a linear dependence between the hydrogen volume and the reaction time (ammonia borane conversion less than $45\pm5\%$). Considering H₂O in large excess, this suggests pseudo-zero order kinetics with respect to ammonia borane for this reaction. Hence, the corresponding initial hydrogen generation rate (r_{initial}) was calculated based on the slope of the linear part for each curve in Figure S2. In addition, the monometallic Co/CNT was also evaluated for this reaction and almost no activity was found, as shown in Figure S3. Figure 1a displays the catalytic activity of these catalysts, which the Cl-containing Ru_{Cl}/CNT catalysts from our previous study were also used as references for comparison. Obviously, there was a significant increase in catalytic activity for the Cl-free bimetallic RuCo/CNT catalysts compared with the Cl-containing monometallic Ru_{Cl}/CNT catalysts of similar particle size, especially for Ru₁Co/CNT with an r_{initial} of 667.7 mol_{H2}·mol_{Ru}·min⁻¹, which demonstrates a 3.6-fold increment in catalytic activity.



Figure 1. (a) The initial catalytic activity ($r_{initial}$), (b) activation energy (E_a) and the logarithm of preexponential factor (lnA), (c) kinetic isotope effect (KIE) values, and (d) Ru⁰ $3p_{3/2}$ binding energy of the Ru_{Cl}/CNT, Ru₃Co/CNT, Ru₂Co/CNT, and Ru₁Co/CNT catalysts. The Ru loading for Ru_{Cl}/CNT was 1.5 wt%. (e) The charge density difference and corresponding charge transfer of the RuCo catalyst. The yellow and light blue isosurfaces denote the electron increase and depletion zone, respectively.

To gain more insight, the catalysts were kinetically analyzed by varying the reaction temperature from 25 to 40 °C, and the results are shown in Figure S2. The catalysts still retained a linear increase in hydrogen volume with reaction time in the initial stage (ammonia borane conversion less than $45\pm5\%$), confirming the pseudo-zero order kinetics in this temperature range. Similarly, the reaction rate (r) and rate constant (k_H) were calculated, which further yielded the activation energy (E_a) and the logarithm of pre-exponential factor (lnA) based on the corresponding Arrhenius plot. As shown in Figure 1b, the Cl-free bimetallic RuCo/CNT catalysts delivered much lower E_a values compared with the Cl-containing monometallic Ru_{Cl}/CNT catalyst, consistent with the trend of catalytic activity. Moreover, there were slight increases in the E_a for these Cl-free bimetallic RuCo/CNT catalysts with the addition of Co. Hence, Ru_1Co/CNT , with the highest catalytic activity, showed a relatively higher E_a, indicating the effects of another important factor. Based on the Arrhenius equation, both the E_a and $\ln A$ contribute to the reaction rate constant, as the representation of the activation (ΔH^{0^*}) and adsorption (ΔS^{0^*}) of reactants over the catalyst surface, respectively⁴²⁻⁴⁴. As shown in Figure 1b, the higher $\ln A$ of $\operatorname{Ru}_1\operatorname{Co/CNT}$ corresponds to the lower loss of translational freedom upon reactant adsorption as a result of weaker interactions between the catalyst surface and reactants. This is consistent with our previous study⁴³ that Ru locates at the left side of the volcanic curve owing to strong interactions with reactants, and weakening this interaction gives rise to higher catalytic activity.

Kinetic isotopic experiments replacing H_2O with D_2O as the reactant were also conducted to probe the underlying kinetic information. As shown in Figure S4, all these catalysts still displayed a linear increase in hydrogen volume with reaction time in the initial stage (ammonia borane conversion less than $45\pm5\%$), but much slower hydrogen generation rate when using D_2O as the reactant. Similarly, the corresponding reaction rate constant (k_D) was calculated based on the slope of the linear part for each curve. As a result, the ratio of the reaction rate constant using H_2O and D_2O as reactant, that is, k_H/k_D , was calculated, which has been widely used to study the kinetic isotope effect (KIE). As shown in Figure 2c, the Cl-free bimetallic RuCo/CNT catalysts delivered lower KIE values compared with the Cl-containing monometallic Ru_{Cl}/CNT catalyst, which suggests that the presence of Cl may inhibit water activation. By contrast, further increasing Co loading gave rise to a relatively higher KIE value, in line with the activation energy trend in Figure 2b.

3.2. Structural characterization

High-resolution transmission electron microscopy (HRTEM) was first employed to probe the significantly improved hydrogen generation kinetics. As shown in Figure S5, it was clear that the Cl-free bimetallic Ru-Co catalysts exhibited the inter-spacings ranging from 0.213 to 0.209 nm and from 0.221 to 0.217 nm, most likely attributed to the (002) and (100) facets of the RuCo alloy, respectively. H₂-TPR measurement was conducted to characterize these catalysts. As shown in Figure S6, all these catalysts exhibited one main hydrogen consumption peak ascribed to the reduction of Ru species. Specifically, with respect to the Cl-containing monometallic Ru_{Cl}/CNT catalyst, the hydrogen reduction peak shifted from the higher temperature of 213 °C to lower temperatures for these RuCo/CNT catalysts. Generally, the reduction temperature of a metal varies according to the interaction between the metal precursor and catalyst support. Hence, the observed decrease in reduction temperature indicates lower stability of the Cl-free Ru precursor, either intrinsically less stable or stabilized by the support. By contrast, the reduction peak gradually shifted to a relatively high temperature with the addition of Co, attributed to the strong Ru and Co interactions. Notably, the absence of legible Co reduction peaks for these catalysts could be ascribed to the high dispersion of Co atoms within the Ru-Co alloy particles, which could be easily reduced by the spillover hydrogen from Ru sites.

XPS was further employed to characterize the electronic properties of these catalysts. As shown in Figure S7, the Cl-free bimetallic RuCo/CNT catalysts exhibited much stronger XPS peak intensities compared with the Cl-containing monometallic Ru_{Cl}/CNT catalyst, possibly due to differences in the Ru precursor. The XPS Ru $3p_{3/2}$ spectra was further deconvoluted into three Ru species, Ru^0 , Ru^{2+} and Ru^{4+} , to gain a more detailed quantitative understanding. It was found that metallic Ru (Ru^0) remained the primary Ru species for these catalysts. Interestingly, there was a downshift in Ru binding energy for these catalysts, as shown in Figure 1d, following the order of Ru_{Cl}/CNT (462.85 eV) > Ru_3Co/CNT (462.65 eV) > Ru_2Co/CNT (462.61 eV) > Ru_1Co/CNT (462.60 eV). Considering the similar metal particle size of these catalysts, the observed binding energy shift was mainly ascribed to electron transfer within the catalysts. Specifically, Co as an electron donor would transfer more electrons to Ru and gave rise to lower Ru binding energy. To verify this, DFT calculations were carried out to probe the electron transfer between Ru and Co. Figure 1e displays the 3D electron density of the Co-doped Ru(001) facet and showed increased electron density around the Ru atoms in comparison with decreased density around the Co atoms. As a result, the Ru charge based on Bader charge analysis was determined to be 0.07 e and 0.04 e, which is in line with the XPS results of the electron transfer from Co to Ru.

Based on our previous study⁴³, the monometallic Ru was found to be less active and located on the left side of the volcanic curve owing to the strong interactions with reactants, this is Ru⁺-H⁻-BH₂NH₃. To weak this interaction toward the top of the volcanic curve, it is necessary to increase the Ru electron density by lowering its binding energy. Hence, from an electronic properties point of view, the addition of Co could effectively lower the Ru binding energy, which should give rise to increased catalytic activity. In this regard, a correlation between the Ru⁰ $3p_{3/2}$ binding energy and r_{initial} was made as shown in Figure 2. The catalytic activity of these catalysts exhibited a sharp increase and followed two linear relationships with the Ru⁰ $3p_{3/2}$ binding energy for which the amplitude of variation induced by Cl was much more significant than that induced by Co. This suggested that, apart from the electronic effects, other effects (e.g., geometric effects) induced by Cl may significantly contribute to the improved catalytic activity when using the Cl-free Ru precursor.



Figure 2. The relationship between $r_{initial}$ and the $Ru^0 \ \beta p_{3/2}$ binding energy for the Ru_{Cl}/CNT , Ru_3Co/CNT , Ru_2Co/CNT , and Ru_1Co/CNT catalysts. The Ru loading for Ru_{Cl}/CNT was 1.5 wt%.

3.3. Decoupling the electronic and geometric effects

To better illustrate the influence of Cl, DFT calculations were first carried out to investigate the adsorption of Cl and its results on three representative Ru facets, Ru(001), Ru(101) and Ru(111). The electron density around Cl was obviously depleted for these three facets, and Cl as an electron donor to transfers electrons to Ru. As a result, the Bader charge analysis suggests that the Ru(001), Ru(101) and Ru(111) facets capture 0.53 e, 0.54 e and 0.48 e from Cl, respectively. Hence, the electron-rich Ru is inconsistent with its low catalytic activity, which indicates that the electronic effects are not the main reason for the significant improvement seen when using a Cl-free Ru precursor. Moreover, Figure 3a shows that these three facets exhibit strong Cl adsorption, especially for the stepped Ru(111) facet with an adsorption energy of 3.43 eV. Considering that the Ru edge site was identified as the main active site for this reaction, the strongest adsorption of Cl on the edge-like Ru(111) facet indicates the severe blockage and significant loss of Ru active sites.



Figure 3. (a) The adsorption energy of Cl and corresponding isosurfaces of the differential electron density for Cl on the Ru(001), Ru(101) and Ru(111) facets. The yellow and light blue isosurfaces correspond to the zones of electron increase and depletion, respectively. (b) The energy profiles and corresponding structures of transition states for H₂O activation over the Ru(111) and Ru(111)-Cl facets. (c) The XPS Cl 2p spectra, (d) H₂-TPR profiles, (e) hydrogen generation volume as a function of reaction time using H₂O and D₂O as reactant, and (f) initial catalytic activity (r_{initial}) for the Ru_{Cl}/CNT and Ru/CNT catalysts. The Ru loading for Ru_{Cl}/CNT was 1.5 wt%.

Furthermore, the influence of Cl adsorption on the neighboring Ru active site was also studied. Considering the substantial kinetic isotope effect (KIE), as shown in Figure 1c, the adsorption and activation of H₂O on Ru(111) and Cl-doped Ru(111), that is, the Ru(111)-Cl facet, were comparatively investigated through DFT calculations. Figure S8 displays the optimized most stable adsorption configurations of the involved species on the Ru(111) and Ru(111)-Cl surfaces, and the corresponding potential energy profiles are displayed in Figure 3b. The adsorption energy of H₂O on the Ru(111) surface was higher than that on the Ru(111)-Cl surface. As a result, the energy barrier for H₂O activation on the Ru(111) and Ru(111)-Cl surfaces were calculated to be 0.63 and 0.67 eV, respectively. This indicates that the Ru(111)-Cl surface had less stable interactions with H₂O and poorer activity for H₂O dissociation. To gain additional insight, the structures of the transition state over these two surfaces were further compared (Figure 3b). It can be seen that the absence of Cl helped to remove the effect of steric hindrance and elongated the H-O bond from 1.40 to 1.44 Å within H₂O, promoting its dissociation. Hence, from the point view of geometric effects, it can be predicted that the absence of Cl would not only inhibit blockage of the active site but also eliminate the effect of steric hindrance in water dissociation. To verify this prediction, the Cl-free monometallic Ru catalyst, Ru/CNT, was prepared by using $\operatorname{Ru}(\operatorname{NO})(\operatorname{NO}_3)_3$ as the precursor, thus isolating the effects of Co to enable a fair comparison with the $\operatorname{Ru}_{\operatorname{Cl}}/\operatorname{CNT}$ catalyst. As shown in Figure S9, the HAADF-STEM image of the Ru/CNT catalyst exhibited a relatively homogeneous distribution of Ru particles, the average particle size of which was determined to be 1.34 ± 0.29 nm. The similar metal particle sizes of the Ru/CNT and Ru_{Cl}/CNT catalysts would help to exclude effects of the Ru size in this reaction. Moreover, the XPS Cl 2p spectra in Figure 3c showed that the Cl-containing Ru_{Cl}/CNT catalyst demonstrates a legible peak with respect to the Cl-free Ru/CNT catalyst, indicating the presence of residual surface Cl species despite H₂reduction. H₂-TPR measurements were further conducted to probe the influence of the residual surface Cl species on the reducibility of Ru species. As shown in Figure 3d, the H₂-TPR profiles were consistent with the above results (Figure S6) in which the Cl-free Ru/CNT catalyst exhibited a lower hydrogen reduction peak than the Cl-containing Ru_{Cl}/CNT catalyst exhibited a lower close results (Figure S6) in which the Cl-free Ru/CNT catalyst exhibited a lower hydrogen reduction peak than the Cl-containing Ru_{Cl}/CNT catalyst exhibited a lower hydrogen reduction.

The as-obtained Cl-free monometallic Ru/CNT catalyst was tested for this reaction by using either H₂O or D₂O as the reactant. As shown in Figure 3e, the catalyst exhibited a lower reaction rate when using D₂O as the reactant compared to H₂O. According to the above method, the KIE value for Ru/CNT was determined to be 3.15, compared with that of 3.35 for Ru_{Cl}/CNT. The decreased KIE value for Ru/CNT is consistent with the above DFT calculations for eliminating site blockage and steric hindrance in water dissociation. Furthermore, the initial catalytic activity of Ru/CNT was determined to be 642.8 mol_{H2}·mol_{Ru}⁻¹·min⁻¹, which is 3.5-fold higher than that of the Ru_{Cl}/CNT catalyst. Taken together, these findings indicate that the influence of Cl is mainly attributed to geometric effects, including site blockage and steric hindrance, which are much more significant than the electronic effects of Co, as shown in Figure 2.

3.4. Maximizing catalytically active sites

Based on the above analysis, the Cl geometric effects and Co electronic effects are likely to give rise to the 3.5- and 0.1-fold increment in catalytic activity, respectively, which the geometric effects are much more significant than the electronic effects in terms of Ru local structure. Hence, for catalyst design, it is highly desirable to further convert the Co electronic effects into geometric effects. Herein, a strategy of acid leaching is proposed to treat the above Cl-free bimetallic Ru-Co catalysts, as shown in Figure 4, with the aim of removing inactive Co sites and creating more edge-like Ru active sites. The removal of Co atoms creates vacancies on the surface of the metal particles, giving rise to low-coordinated Ru atoms in the surrounding area. However, it is difficult to predict the effects of low-coordinated Ru atoms in this reaction. Therefore, a preliminary investigation via DFT calculations was conducted to probe whether the catalytic activity could be promoted by introducing low-coordinated Ru atoms.



Figure 4. The schematic diagram for the preparation of acid-leached al-RuCo/CNT catalyst.



Figure 5. The structure of Ru(001), Ru(001)-1, Ru(001)-3, and Ru(001)-Co facets.

To simulate the process of acid leaching, three (4×4) slab models of the typical Ru facet, Ru(001), with different vacancy numbers (0, 1, and 3), i.e., Ru(001), Ru(001)-1, and Ru(001)-3, were constructed as shown in Figure 5, which the Ru(001) facet with partial Co replacement, Ru(001)-Co, was also used as a reference. With respect to the Ru(001) facet, the coordination number of six Ru atoms within the Ru(001)-1 facet decreased and that of nine Ru atoms decreased in the Ru(001)-3 facet. Thus, it is reasonable to deduce that the increased Co content within the bimetallic Ru-Co catalyst would contribute to more low-coordinated Ru sites after the removal of Co. In light of the above analysis on H₂O dissociation as the prerequisite for H₂ production over Ru catalysts, the energy profiles and corresponding adsorption configurations of the involved species for H₂O activation over these surfaces were comparatively studied, as shown in Figures 6a, 6b and S10. The activation barrier for H₂O dissociation followed a clear trend of Ru(001) (0.89 eV) > Ru(001)-Co (0.80 eV) > Ru(001)-1 (0.77 eV) > Ru(001)-3 (0.70 eV). It can be seen that activation energy decreased with the number of low-coordinated Ru sites. Therefore, based on the DFT calculations, the removal of Co atoms from the bimetallic RuCo/CNT catalyst could create more low-coordinated Ru sites with higher catalytic activity for water dissociation, thus promoting H₂ production from ammonia borane.



Figure 6. (a) The energy profiles, and (b) corresponding structure of transition states for H_2O activation

on the Ru(001), Ru(001)-1, Ru(001)-3 and Ru(001)-Co facets. (c) The Ru and Co loading for the bimetallic Ru-Co catalysts before and after acid leaching. (d) The XPS Ru $3p_{3/2}$ spectra of acid-leached al-RuCo/CNT catalysts.

The above findings support the prediction that the removal of Co sites can create more low-coordinated Ru active sites for this reaction. To further investigate this, dilute HNO_3 (0.01 M) was chosen to treat the catalysts to selectively remove Co atoms because concentrated HNO₃ may dissolve Ru atoms. The contents of Ru and Co species in the spent acid solution were measured by ICP. It was found that the contents of Ru in all spent acid solutions were lower than the detection limit. By contrast, the contents of Co in the spent acid solutions varied with the identity of catalyst, based on which the contents of residual Co in the acid-leached catalysts (al-RuCo/CNT) were determined as shown in Figure 6a. Nearly all the Co species within the catalysts were dissolved into the acid solution, indicating the successful removal of Co, rather than Ru, for these al-RuCo/CNT catalysts. HAADF-STEM was employed to characterize these catalysts to investigate the influence of acid leaching on the metal particle sizes and distributions. As shown in Figure S11, all catalysts retained a relatively homogeneous distribution of metal particles and were nearly unchanged in size compared to them before the acid leaching treatment. XPS measurement was also conducted to probe changes in the catalysts before and after acid leaching, and the results are shown in Figure 6d. All catalysts clearly exhibited significant increases of 0.3-0.4 eV in the Ru binding energy after acid leaching. This is consistent with Co transferring electrons to Ru and the removal of Co lowering the electron density of Ru to increase its binding energy.



Figure 7. (a) The hydrogen generation volume as a function of reaction time, (b) the initial catalytic activity ($r_{initial}$), (c) the activation energy (E_a) and logarithm of pre-exponential factor ($\ln A$) for the al-Ru₃Co/CNT, al-Ru₂Co/CNT, al-Ru₁Co/CNT, and Ru_{Cl}/CNT catalysts. (d) The relationship between

activation energy (E_a) and the logarithm of pre-exponential factor $(\ln A)$ of the above catalysts. The Ru loading for Ru_{Cl}/CNT catalyst was 1.5 wt%.

The acid-leached catalysts were tested for this reaction under the same reaction conditions, and the results are shown in Figure 7a. All catalysts still retained zero-order kinetics at the initial stage of the reaction, and the initial catalytic activity ($r_{initial}$) was further calculated as shown in Figure 7b. As expected, all catalysts demonstrated a sharp increase in catalytic activity. Notably, the highest hydrogen generation of 751.0 mol_{H2}·mol_{Ru}⁻¹·min⁻¹was achieved for the al-Ru₁Co/CNT catalyst, which was almost 4.1-fold higher than that of the Ru_{Cl}/CNT catalyst. Kinetic experiments over the temperature range from 25 to 40 °C were also performed, as shown in Figure S12. Similarly, the reaction rate constants at different temperatures could be calculated, which further yielded the activation energy (E_a) and the logarithm of pre-exponential factor (lnA). Figure 7c shows that both E_a and lnA decreased with the Co content within the bimetallic RuCo/CNT catalyst before acid leaching. This is consistent with the above DFT calculations showing that the more low-coordinated Ru sites after acid leaching, the lower the activation energy for the kinetically relevant step of water dissociation.

Furthermore, it is found that the kinetics parameters E_a and $\ln A$ demonstrated a remarkable kinetic compensation effect, as shown in Figure 7d, which followed the Cremer-Constable relation of a linear dependence of $\ln A$ on E_a ^{45,46}. This compensation effect could be divided into three kinetics regimes: the al-RuCo/CNT, RuCo/CNT, and Ru_{Cl}/CNT catalysts located in the regimes of low, medium and high E_a and $\ln A$ values, respectively. In light of the previous DFT study, this could be interpreted as the change in the binding strength of reaction species, which induces a switch in the kinetic regime. Specifically, the adsorption of reactants could be weak for the Cl-containing Ru_{Cl}/CNT catalyst due to site blockage and steric hindrance. Upon the removal of Cl and the introduction of low-coordinated Ru active sites, the reaction switches from a Cl coverage-limited regime to a reactant activation regime, giving rise to al-RuCo/CNT catalysts with lower activation energies that have higher catalytic activity. Hence, combining the DFT calculations, multiple characterizations, and kinetic analyses allow the conclusion that the presence of abundant low-coordinated Ru sites after acid leaching contribute to a significantly increased quantity and quality of Ru active sites, thereby boosting the catalytic activity of al-Ru₁Co/CNT. The mechanistic insights gained through this study may serve as a foundation for fine-tuning the metal local structure to achieve enhanced reaction kinetics.

4. Conclusions

In summary, we demonstrated a strategy for engineering Ru local structures via the employment of a Clfree Ru precursor and the acid leaching of bimetallic Ru-Co catalysts, toward more active site with high mass-specific activity for hydrogen generation from ammonia borane hydrolysis. The roles of Cl and Co were separately investigated by comparing Cl-free/Cl-containing monometallic Ru catalysts and Co-leaching/Cocontaining bimetallic Ru-Co catalysts, respectively. A combination of multiple characterization techniques, kinetic (isotopic) analyses, and DFT calculations suggests that the influences of Cl and Co are mainly attributed to geometric effects (site blockage and steric hindrance) and electronic effects (electron transfer from Co to Ru), respectively. Decoupled from other factors, the Ru geometric effects were identified as the main factor for improving the hydrogen generation rate, which could be further promoted by acid leaching to introduce more low-coordinated Ru sites. It is found that the quantity of edge-like Ru active sites increased with the Co content in bimetallic Ru-Co catalysts, giving rise to a significantly lower activation barrier for water dissociation. As a result, the acid-leached al-Ru₁Co catalyst with the increased quantity and quality of Ru active sites delivered a substantial 4.1-fold increase in catalytic activity. The strategy developed here may shed new light on the design and fabrication of metal catalysts with the maximum active sites for this reaction.

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