

Supplementary Materials

**Kinetics-assisted discrimination of active sites in Ru catalyzed
hydrolytic dehydrogenation of ammonia borane**

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DFT Calculations

The DFT calculations were performed by employing the Vienna Ab-initio Simulation Package (VASP). The interaction between the valence electrons and the core was described by projected augmented wave (PAW) method, and the exchange-correlation functional was GGA-PBE. The Kohn-Sham orbitals were expanded in a plane wave basis set with a kinetic cutoff energy of 450 eV. The sampling of the Brillouin zone was performed using a Monkhorst-Pack scheme, and electronic occupancies were determined in light of a Methfessel-Paxton scheme with an energy smearing of 0.2 eV.

We obtained a DFT-determined equilibrium lattice constant of $a=2.72 \text{ \AA}$ and $c=4.31 \text{ \AA}$ for bulk Ru in the hcp structure, which agrees well with the experimental bulk lattice constant ($a=2.71 \text{ \AA}$ and $c=4.28 \text{ \AA}$)^[1]. The surface slabs of Ru(001), Ru(101) and edge liked Ru(111) were modeled with $p(4 \times 4)$, $p(2 \times 4)$ and $p(4 \times 4)$ supercells, respectively. To minimize the interactions between the slabs, we employed a vacuum region with a $15 \text{ \AA}$ thickness. For the calculation of surfaces and adsorption species, bottom two-layered Ru were fixed and the top two-layered Ru as well as the adsorbates were relaxed.

The adsorption energy (E_{ads}) is determined by Eqs. 1.

$$E_{\text{ads}} = E_{(\text{H}_2\text{O}+\text{surface})} - E_{(\text{H}_2\text{O})} - E_{(\text{surface})} \quad (1)$$

where $E_{(\text{H}_2\text{O}+\text{surface})}$, $E_{(\text{H}_2\text{O})}$ and $E_{(\text{surface})}$ are the energies of water on the surface, adsorbates in gas phase and the surface, respectively.

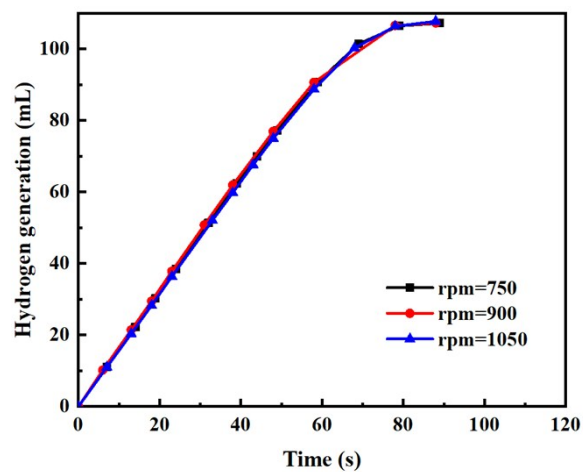


Fig. S1 Hydrogen generation volume as a function of time under different stirring speeds over 0.2g Ru-0.75 catalyst at 30 °C.

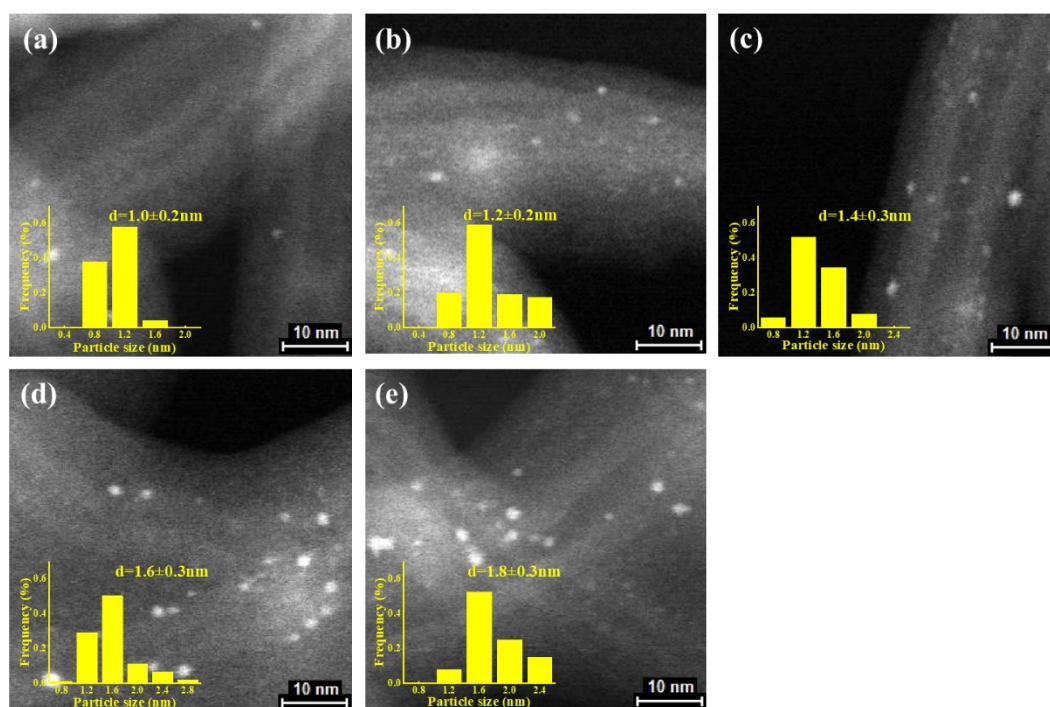


Fig. S2 Typical HAADF-STEM images of Ru/CNT catalysts with different Ru loadings and the corresponding size distributions: (a) Ru-0.5, (b) Ru-0.75, (c) Ru-1.5, (d) Ru-4.5 and (e) Ru-6.0.

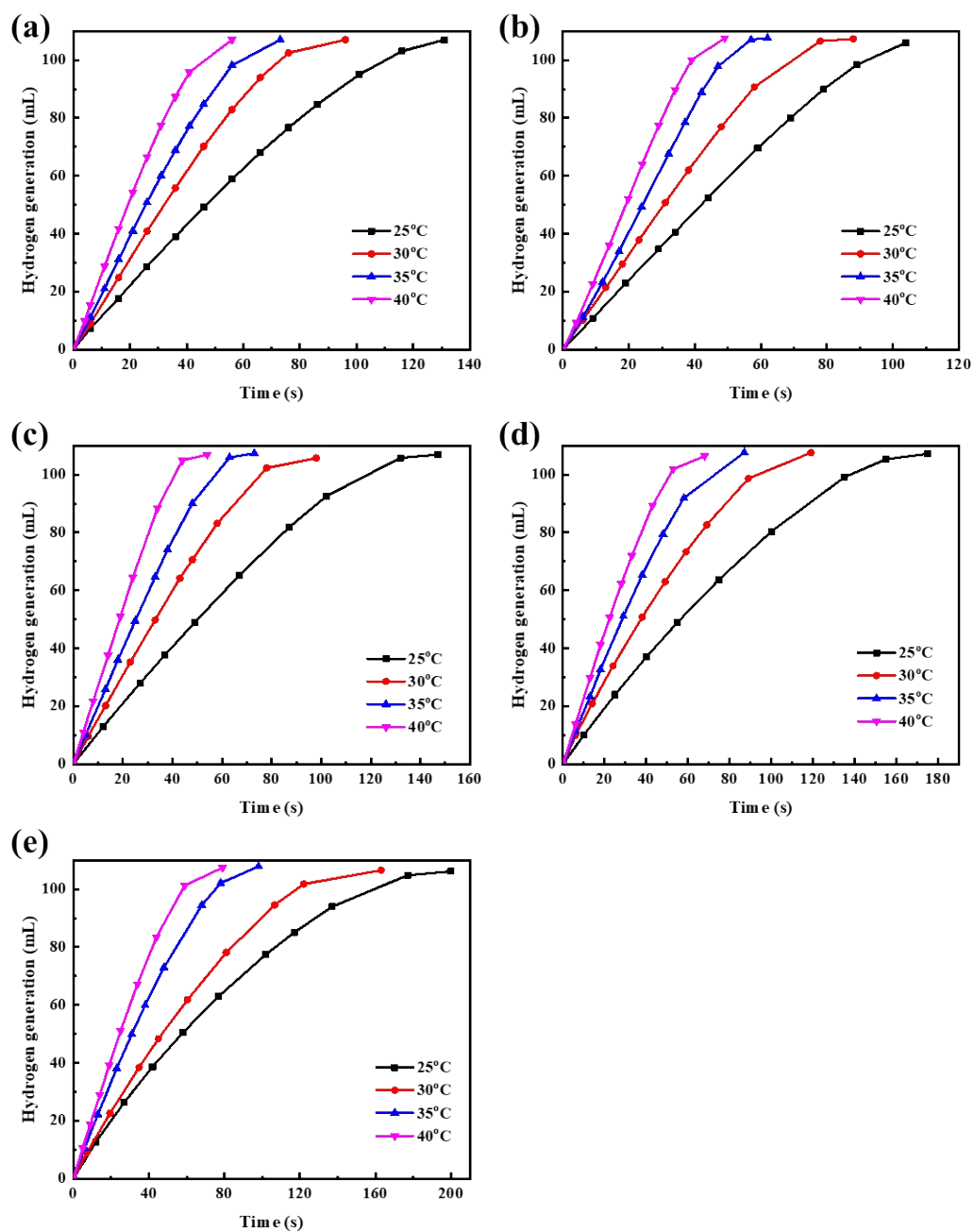


Fig. S3 Hydrogen generation volume as a function of time over differently sized Ru/CNT catalysts at 25, 30, 35, and 40 °C: (a) Ru-0.5, (b) Ru-0.75, (c) Ru-1.5, (d) Ru-4.5 and (e) Ru-6.0.

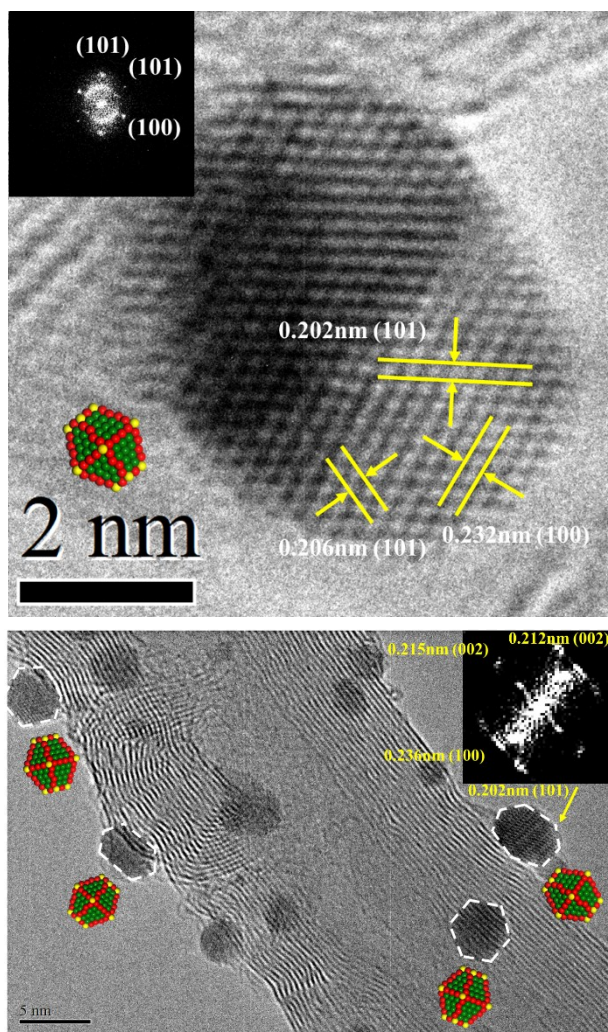


Fig. S4 Typical HRTEM images of Ru nanoparticles supported on CNT.

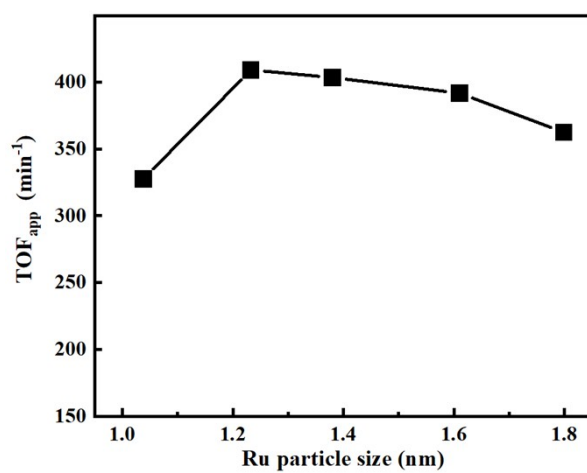


Fig. S5 Plots of the appearance turnover frequency at 30 °C with Ru particle size.

Table S1. Formulas to calculate the atom numbers at different positions for each Ru particle^[2].

Total atom number of each particle (N_T)	$0.25(14m^3-21m^2+14m-4)$
Surface atom number of each particle (N_S)	$7.5m^2-14m+6$
Corner atom number of each particle (N_{corner})	12
Edge atom number of each particle (N_{edge})	$18m-40$
001 atom number of each particle (N_{001})	$1.5(m-2)^2$
101 atom number of each particle (N_{101})	$6m^2-26m+28$

Note:

The diameter of Ru atom ($d_{\text{Ru atom}}$) is 0.268 nm, and the particle size with the total atoms (N_T) in one truncated bipyramid follows the relationship of $1.105 \times N_T^{1/3} \times d_{\text{Ru atom}}$. m is the number of atoms lying on an equivalent edge (corner atoms included), and five different Ru/CNT catalysts in this study have $m = 2.775, 3.212, 3.544, 4.058$ and 4.481 , respectively. Due to the Ru particle is lie along the cone axis direction, resulting the coverage of 1/3 number of $\{101\}$ facets, edge and corner atoms, and the calculated formulas of the atom numbers at different positions for each Ru particle was summarized in Table S1.

The fraction of each typed active site per mole of Ru y_i can be calculated by (taking edge atoms for example):

$$y_{\text{edge}} = \frac{N_{\text{edge}}}{N_{\text{Total}}} = \frac{18m - 40}{0.25(14m^3 - 21m^2 + 14m - 4)} \quad (2)$$

For each reaction (5ml 0.01g·mL⁻¹AB), the molar ratio of Ru to AB is the same. With the same mole of Ru (n_{Ru}), the particle numbers for different sized Ru/CNT (N_p) can

be calculated by:

$$N_p = n_{Ru} \cdot N_A / N_T = (0.0015 / M_{Ru}) \cdot N_A / N_T \quad (3)$$

where N_A is the Avogadro constant and M_{Ru} is the molecular weight.

The initial hydrogen generation rate can be calculated by:

$$r_{\text{initial}} = n_{H_2} / (t \cdot n_{Ru}) \quad (4)$$

Where t is the reaction time.

The apparent TOF_{app} can be calculated as:

$$TOF_{\text{app}} = r_{\text{initial}} \cdot n_{Ru} \cdot N_A / (N_{\text{surface}} \cdot N_p) = r_{\text{initial}} / y_{\text{surface}} \quad (5)$$

The corresponding TOF_i (turnover frequency of specific active site) can be obtained as:

$$TOF_i = r_{\text{initial}} \cdot n_{Ru} \cdot N_A / (N_i \cdot N_p) = r_{\text{initial}} / y_i \quad (6)$$

The TOF_i is normalized to the highest $TOF_{i, \text{max}}$ for each type of active site as follows:

$$TOF_{i, \text{Normalized}} = TOF_i / TOF_{i, \text{max}} \quad (7)$$

Reference

1. Y. Pan, H. G. Zhang, D. X. Shi, J. T. Sun, S. X. Du, F. Liu, H. J. Gao, Adv. Mater., 2009, 21(27), 2777.
2. R. V. Hardeveld, F. Hartog, Surf. Sci., 1969, 15(2), 189.