The electronic supplementary information for

Metal-acid site synergistic catalysis in Ru–ZrO_2 toward selective hydrogenation of benzene to cyclohexene

Deming Rao,‡ Xiaoge Xue,‡ Guoqing Cui, Shan He, Ming Xu, Weihan Bing, Shuxian Shi* and Min Wei*

State Key Laboratory of Chemical Resource Engineering, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China

***** Corresponding authors. Tel: +86-10-64412131; Fax: +86-10-64425385.

E-mail addresses: shisx@mail.buct.edu.cn (S. Shi); weimin@mail.buct.edu.cn (M. Wei).

‡ These authors contributed equally to this work and should be considered as co-first authors.

Computational details

Density functional theory (DFT),[1] as implemented in the Vienna ab initio Simulation Package (VASP),[2] was employed to perform the first-principles calculations. The DFT calculations were performed by using the electron projector-augmented wave methods[3] with the PBE generalized gradient approximation (GGA) exchange-correlation functional,[4] plus an on-site Zr d state U correction (DFT + U, or GGA + U).[5] The value of U = 4.0 was applied for the Coulomb correction to the Zr 4d states, which was reported to well describe the electronic properties and defect states in crystalline Zirconium dioxide.[6-9] The ZrO_2(−111) surface and B-doped ZrO_2(−111) surface with *p* (2×2) supercells are cleaved according to the XRD patterns (Fig. 1 in main manuscript). A plane-wave cut-off of 400 eV was used. The Brillouin zone was sampled using a 3×3×1 Monkhorst-Pack *k*-point mesh.[10] Spin polarization was taken into account in all calculations for comparison. The adsorption energy (E_{ad}) was defined as follows:

$$E_{ad} = E_{total} - (E_{slab} + E_{adsorbate}) \quad (1)$$

where E_{total} is the total energy of adsorbate-slab system; E_{slab} and $E_{adsorbate}$ are the energies of the slab and the gas phase adsorbate, respectively. A negative value of E_{ad} corresponds to an exothermic process.

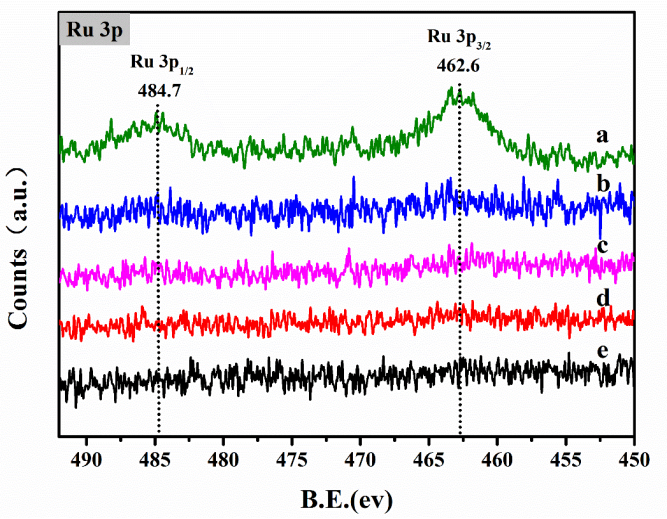

Fig. S1 Ru 3p XPS spectra of (a) Ru/ZrO_2, (b) $Ru/ZrO_2@ZrO_2$-B(0%), (c) $Ru/ZrO_2@ZrO_2$-B(5%), (d) $Ru/ZrO_2@ZrO_2$-B(10%) and (e) $Ru/ZrO_2@ZrO_2$-B(15%), respectively.

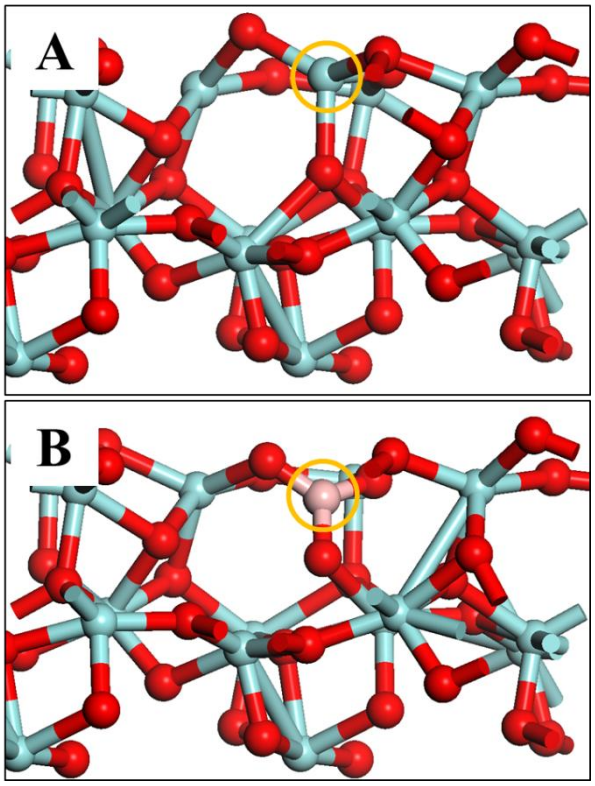

Fig. S2 Sideview of (A) ZrO_2(–111) and (B) B-ZrO_2(–111) facet. The red, cyan and pink ball represents O, Zr and B atom, respectively. The doped B atom and its original position of Zr atom are encircled.

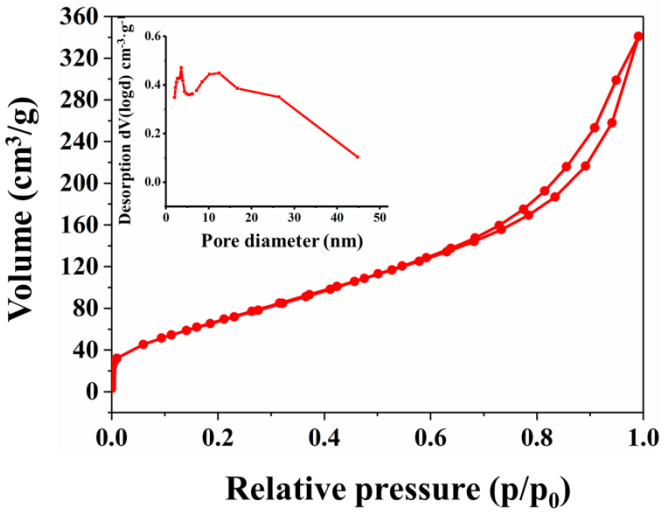

Fig. S3 Nitrogen adsorption-desorption curves and the pore diameter distribution (inset) for the sample of $Ru/ZrO_2@ZrO_2$-B(5%).

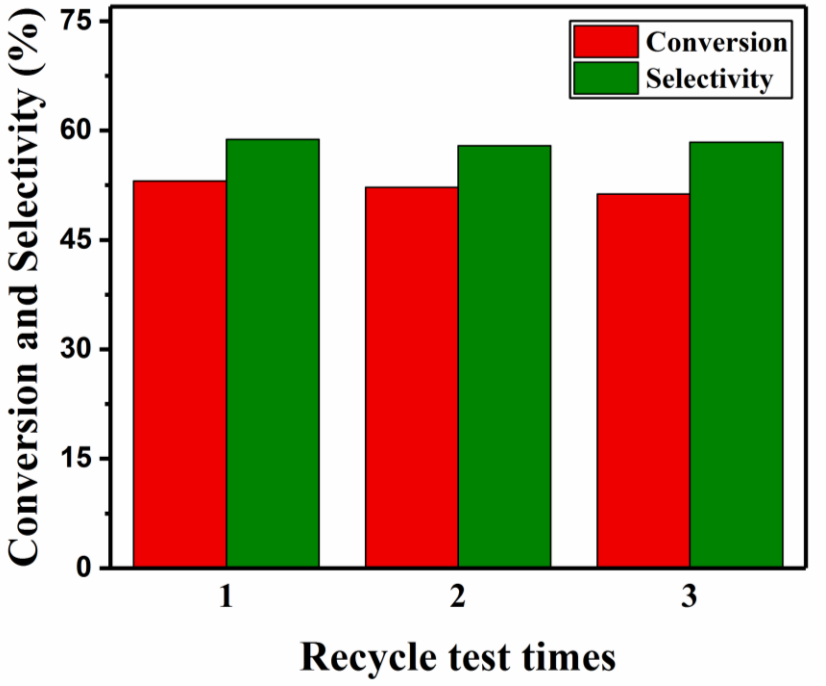

Fig. S4 Catalytic performance of $Ru/ZrO_2@ZrO_2$(5%) in three consecutive recycles.

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