The electronic supplementary information for

Metal-acid site synergistic catalysis in Ru–ZrO₂ toward selective hydrogenation of benzene to cyclohexene

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Computational details

Density functional theory (DFT), as implemented in the Vienna ab initio Simulation Package (VASP), was employed to perform the first-principles calculations. The DFT
calculations were performed by using the electron projector-augmented wave methods with the
PBE generalized gradient approximation (GGA) exchange-correlation functional, plus an
on-site Zr d state U correction (DFT + U, or GGA + U). 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. 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. Spin polarization was taken into
account in all calculations for comparison. The adsorption energy ($E_{ad}$) was defined as follows:

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

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.
Reference


