Electronic Supplementary Information

Structural dynamics of Ru cluster during nitrogen dissociation in ammonia synthesis

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Fig. S1. Kinetic energy partitioning for the Ru-N₂ system thermostated by Nosé–Hoover chain at 523 K. The N-N bond length is controlled to 1.84 Å.
Fig. S2. (a) Total energy probability distributions $P(E, T)$ and (b) the time accumulative averages of mean forces obtained by NVT combined with Nosé–Hoover chain thermostat with a chain length of three (blue line), the Langevin dynamics (red line), and mixed NVE/NVT sampling (green line) at 523 K. The N-N bond length is controlled to 1.84 Å. The probability distributions and mean forces between NVT and mixed NVE/NVT sampling are very similar, indicating that the interference issue due to the coupling the internal degrees of freedom of the cluster with a thermostat in this work is insignificant.
Fig. S3. Calculated average forces for N$_2$ dissociation on Ru$_{19}$ cluster as a function of N-N bond length at different temperatures (unit: K).
Fig. S4. (a) Time accumulative averages of the forces at the N-N bond length varying from 1.24 Å to 1.84 Å and (b) from 2.04 Å to 3.24 Å at 423 K calculated using AIMD. The inset values are the corresponding N-N bond lengths given in Å.
Fig. S5. Time accumulative averages of mean forces at the N-N bond length of 1.84 Å calculated using different initial structures at 523 K. The inserts are the snapshots of initial structures. I, the N-N bond length is 1.44 Å. II, the N-N bond length is 2.04 Å. The silver and blue balls represent Ru and N atoms.
Fig. S6. Specific heat capacity curves of initial (IS), transition (TS), and finals states (FS) of the N$_2$ dissociation on Ru$_{19}$ cluster.