Supporting Information

The calculations reported here are performed by using periodic, spin-polarized DFT as implemented in Vienna ab initio program package (VASP).[1] The electron-ion interactions are described by the projector augmented wave (PAW) method proposed by Blöchl[2] and implemented by Kresse.[3] RPBE functional[4] is used as exchange-correlation functional approximation and a plane wave basis set with an energy cutoff of 400 eV is used. Only gamma point is used for the Brillouin zone sampling. To model the oxygen functional groups, a graphene sheet in a cubic cell with a 26.72x16.04x15.00 Å for x, y, z dimension is used and the periodic condition is employed along the y direction. All atoms in the cell are allowed to relax during the structure optimization and the optimization is stopped when the force residue on the atom is smaller than 0.02 eV/Å. The reaction pathway and barriers are calculated by using the climbing image nudged elastic band (CI-NEB) method.[5] More detailed information such as k points test can be seen in our previous study.[6]The configuration of the doping atoms (B, N and S) is chosen as graphitic type.The binding energy is defined as:

$$\mathbf{E}_{b} = \mathbf{E}_{tot} - \mathbf{E}_{slab} - \mathbf{E}_{C_2H_5}; \quad (1)$$

Where $\mathbf{E}_{tot}$ is the total energy after the binding of C_2H_5 on the catalyst; $\mathbf{E}_{slab}$ is the energy of the catalyst alone; $\mathbf{E}_{C_2H_5}$ is the energy of the ethane radical in the gas phase.The dissociation energy is defined as:

$$\mathbf{E}_{dis} = \mathbf{E}_{tot} - \mathbf{E}_{slab} - \mathbf{E}_{C_2H_6}; \quad (2)$$

Where $\mathbf{E}_{tot}$ is the total energy after the first C-H bond cleavage of ethaneon the catalystresulting in a ethane radical in the gas phase (the final state in Figure S2); $\mathbf{E}_{slab}$ is the energy of the clean slab alone; $\mathbf{E}_{C_2H_6}$ is the energy of the ethane molecule.

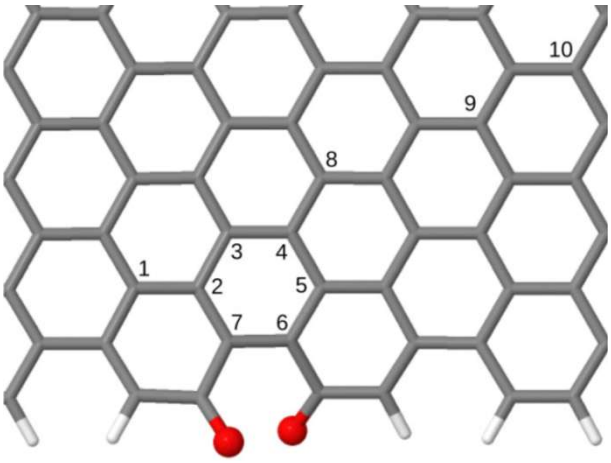

Figure S1: The doping positions on the carbon catalyst. The numbers represent the doping positions. For boron (B) and nitrogen (N) doping,ten positions are calculated; for sulphur(S) doping, only positions marked as 1 and 2 are calculated. Color code: carbon is gray, hydrogen is white, and oxygen is red.

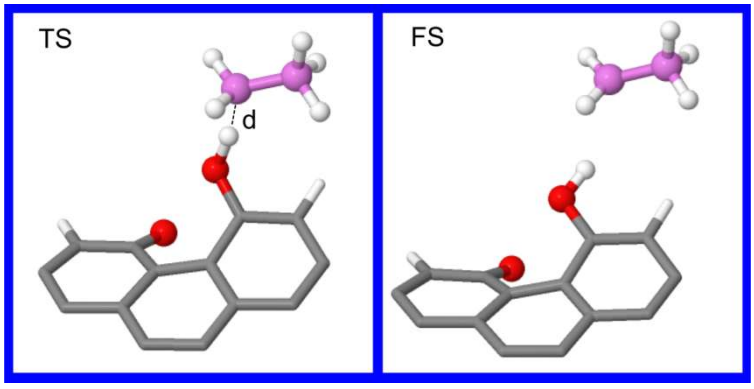

Figure S2:The transition state (TS) and final state (FS) of the first C-H bond cleavage of ethane on the undoped catalyst, in whichd is the length of the C-H bond at the transition state. Color code: carbon on the substrate is gray, carbon in ethane is violet, hydrogen is white, and oxygen is red.

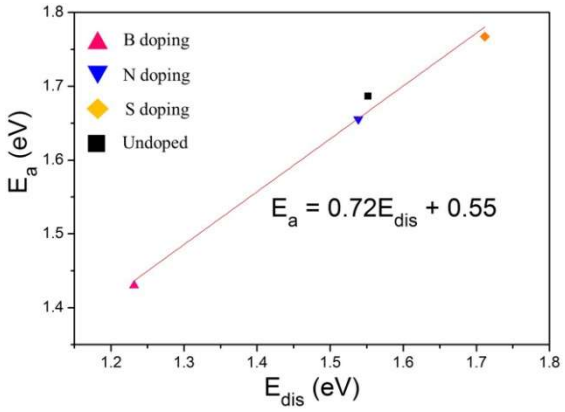

Figure S3: The methane molecule activation on the undoped and doped catalysts and the relation between the dissociation energy (E_{dis}) and the activation energy (E_a). The graphitic dopants are considered in the calculations.

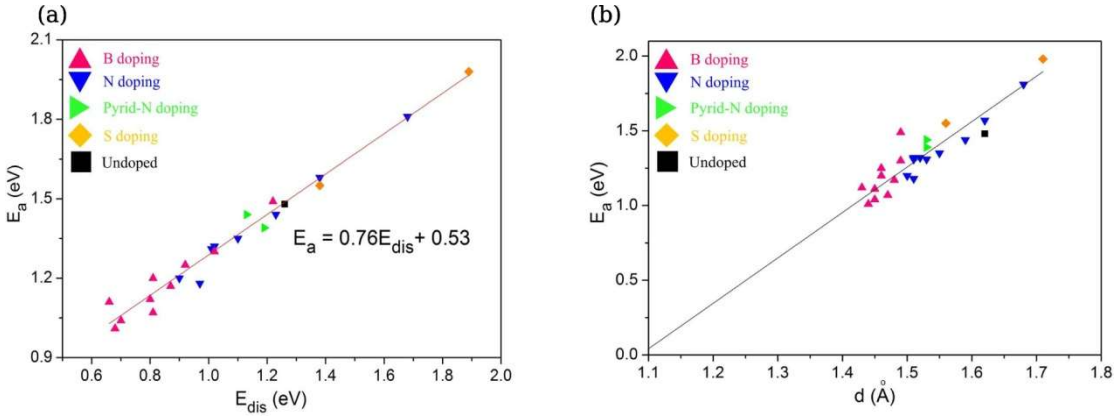

Figure S4: The pyridine nitrogen is included in the data set shown in Figure 2 and 3. (a) The relation between the dissociation energy and the activation energy. (b) The relation between the breaking bond distance and the activation energy.

Table S1：The length (d) of the C-H bond in ethane at the transition state onboth the undoped and doped catalysts, which d is indicated in Figure S2.The unit is Å.

Doping positions	1	2	3	4	5	6	7	8	9	10
undoped					1.57					
B doped	1.48	1.43	1.44	1.45	1.49	1.45	1.47	1.48	1.46	1.46
N doped	1.62	1.59	1.55	1.53	1.51	1.51	1.68	1.52	1.50	1.51
S doped	1.71	1.56								

References

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