

## Supporting Information

### **Support effects on adsorption and catalytic activation of O<sub>2</sub> in single atom iron catalysts with graphene-based substrates**

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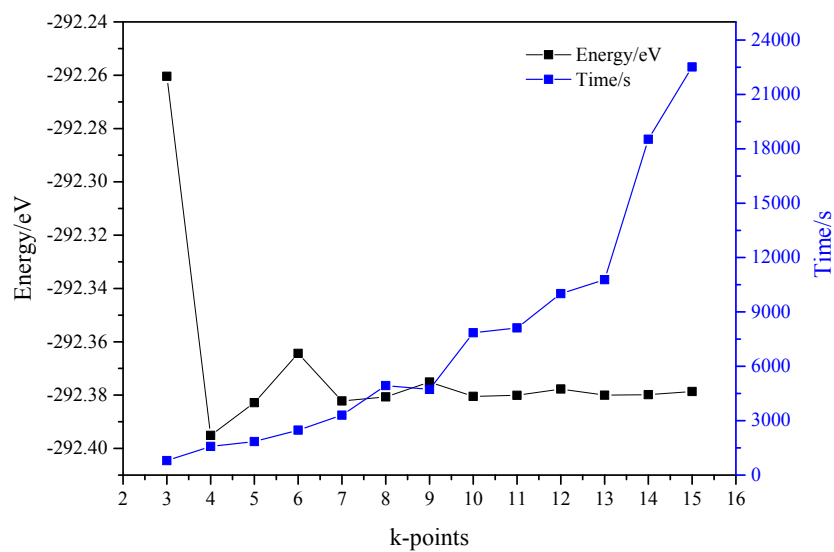
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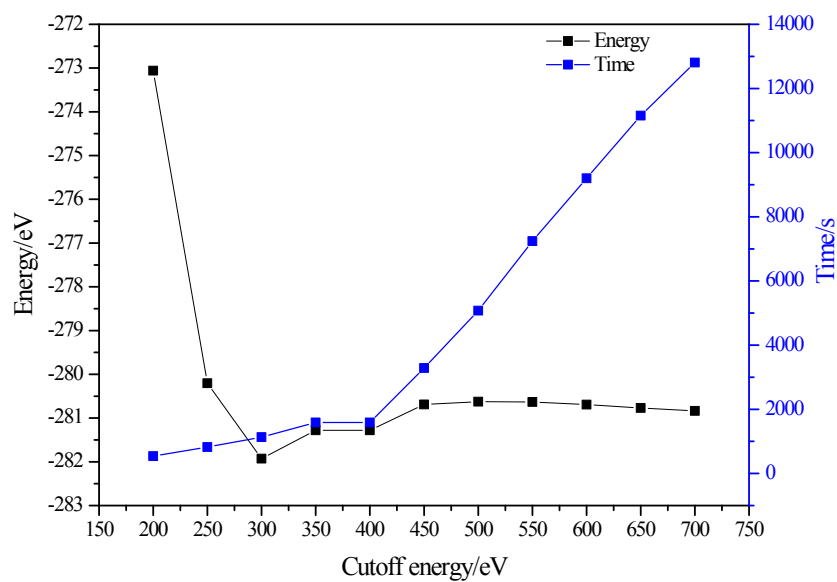
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(a) The convergence test of k-points



(b) The convergence test of cutoff energy

Fig. S1 The convergence test of k-points and cutoff energy

Table S1 The bond length between iron atom and oxygen atom ( $d$ , Å), the bond length between two oxygen atoms ( $d\text{-O}_2$ , Å), the height variation of iron atom ( $\Delta h$ , Å) and the adsorption energy ( $E_{\text{ads}}$ , eV) in the adsorption of  $\text{O}_2$  on Fe/GS

(there are two bonds between iron atom and oxygen atom in side-on adsorption model, which are named as bond-s and bond-l according to the bond length.)

| Fe/GS       | End-on adsorption model |                            |                        |                             | Side-on adsorption model |                          |                            |                        |                             |
|-------------|-------------------------|----------------------------|------------------------|-----------------------------|--------------------------|--------------------------|----------------------------|------------------------|-----------------------------|
|             | $d(\text{\AA})$         | $d\text{-O}_2(\text{\AA})$ | $\Delta h(\text{\AA})$ | $E_{\text{ads}}(\text{eV})$ | $d\text{-s}(\text{\AA})$ | $d\text{-l}(\text{\AA})$ | $d\text{-O}_2(\text{\AA})$ | $\Delta h(\text{\AA})$ | $E_{\text{ads}}(\text{eV})$ |
| Fe/SV-GN    | 1.766                   | 1.287                      | 0.073                  | 1.330                       | 1.852                    | 1.898                    | 1.385                      | 0.125                  | 1.986                       |
| Fe/SV-N1    | 1.763                   | 1.297                      | 0.114                  | 1.219                       | 1.812                    | 1.873                    | 1.402                      | 0.130                  | 2.382                       |
| Fe/SV-N12   | 1.696                   | 1.294                      | 0.077                  | 2.063                       | 1.822                    | 1.823                    | 1.407                      | 0.055                  | 3.038                       |
| Fe/SV-N123  | 1.681                   | 1.288                      | 0.231                  | 2.423                       | 1.824                    | 1.825                    | 1.412                      | 0.334                  | 3.259                       |
| Fe/DV-GN    | 1.703                   | 1.292                      | 0.079                  | 1.271                       | 1.832                    | 1.835                    | 1.387                      | 0.232                  | 1.851                       |
| Fe/DV-N1    | 1.683                   | 1.281                      | 0.237                  | 1.265                       | 1.811                    | 1.857                    | 1.387                      | 0.325                  | 1.603                       |
| Fe/DV-N13   | 1.679                   | 1.284                      | 0.685                  | 1.444                       | 1.871                    | 1.870                    | 1.373                      | 0.775                  | 1.814                       |
| Fe/DV-N14   | 1.894                   | 1.301                      | 0.508                  | 0.721                       | 1.814                    | 1.895                    | 1.369                      | 0.757                  | 1.550                       |
| Fe/DV-N123  | 1.805                   | 1.299                      | 0.532                  | 0.942                       | 1.797                    | 2.007                    | 1.358                      | 0.590                  | 1.188                       |
| Fe/DV-N1234 | 1.836                   | 1.298                      | 0.307                  | 0.764                       | 1.894                    | 1.894                    | 1.357                      | 0.478                  | 0.580                       |

Table S2 The electron transfer characteristics of  $\text{O}_2$  adsorption on Fe/GS

(The plus sign (+) means gain electron, the minus sign (-) means loss electron)

| Fe/GS       | End-on adsorption model         |                                |                                 |                             | Side-on adsorption model        |                                |                                 |                             |
|-------------|---------------------------------|--------------------------------|---------------------------------|-----------------------------|---------------------------------|--------------------------------|---------------------------------|-----------------------------|
|             | $\Delta q\text{-O}_2(\text{e})$ | $\Delta q\text{-Fe}(\text{e})$ | $\Delta q\text{-sub}(\text{e})$ | $E_{\text{ads}}(\text{eV})$ | $\Delta q\text{-O}_2(\text{e})$ | $\Delta q\text{-Fe}(\text{e})$ | $\Delta q\text{-sub}(\text{e})$ | $E_{\text{ads}}(\text{eV})$ |
| Fe/SV-GN    | +0.457                          | -0.247                         | -0.212                          | 1.330                       | +0.616                          | -0.330                         | -0.288                          | 1.986                       |
| Fe/SV-N1    | +0.507                          | -0.298                         | -0.214                          | 1.219                       | +0.677                          | -0.318                         | -0.360                          | 2.382                       |
| Fe/SV-N12   | +0.551                          | -0.251                         | -0.304                          | 2.063                       | +0.699                          | -0.325                         | -0.374                          | 3.038                       |
| Fe/SV-N123  | +0.586                          | -0.276                         | -0.314                          | 2.423                       | +0.746                          | -0.381                         | -0.366                          | 3.259                       |
| Fe/DV-GN    | +0.430                          | -0.076                         | -0.358                          | 1.271                       | +0.570                          | -0.140                         | -0.432                          | 1.851                       |
| Fe/DV-N1    | +0.437                          | -0.013                         | -0.429                          | 1.265                       | +0.573                          | -0.064                         | -0.510                          | 1.603                       |
| Fe/DV-N13   | +0.438                          | -0.019                         | -0.422                          | 1.444                       | +0.573                          | -0.096                         | -0.480                          | 1.814                       |
| Fe/DV-N14   | +0.438                          | -0.085                         | -0.357                          | 0.721                       | +0.561                          | -0.116                         | -0.449                          | 1.550                       |
| Fe/DV-N123  | +0.422                          | -0.106                         | -0.321                          | 0.942                       | +0.570                          | -0.111                         | -0.462                          | 1.188                       |
| Fe/DV-N1234 | +0.447                          | -0.108                         | -0.344                          | 0.764                       | +0.576                          | -0.143                         | -0.436                          | 0.580                       |

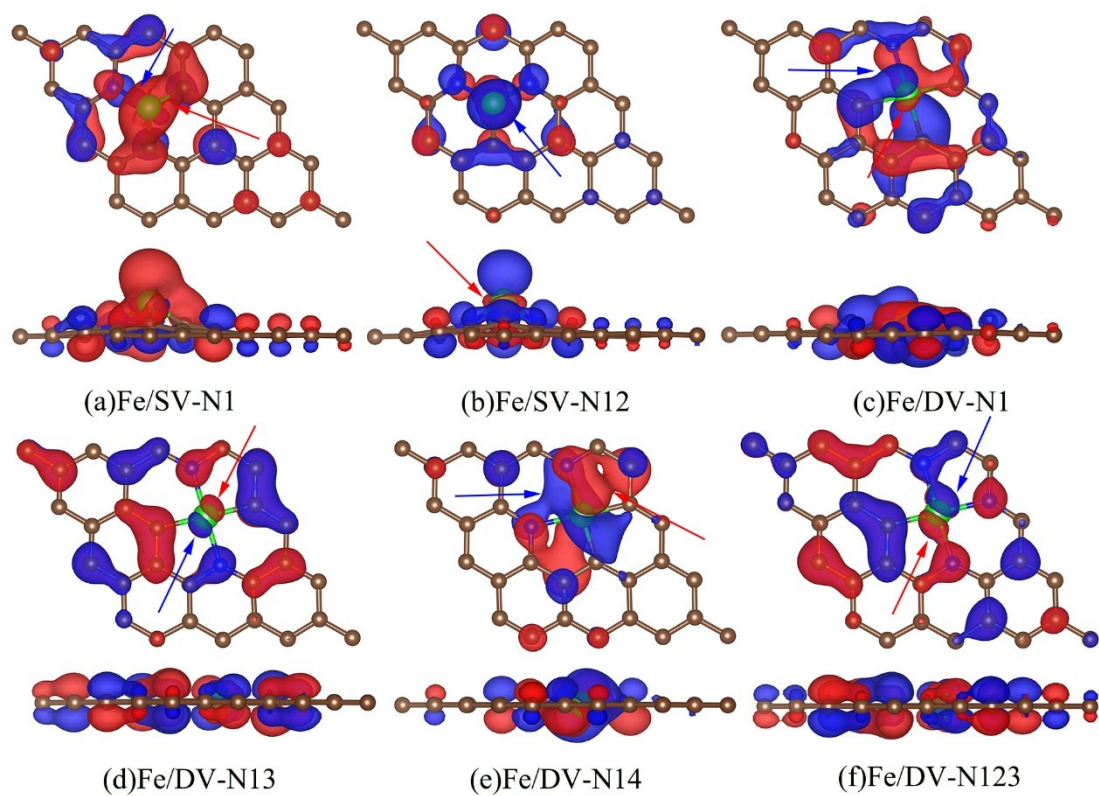
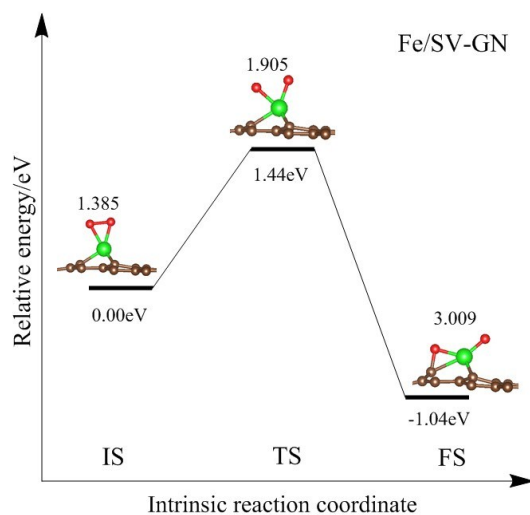


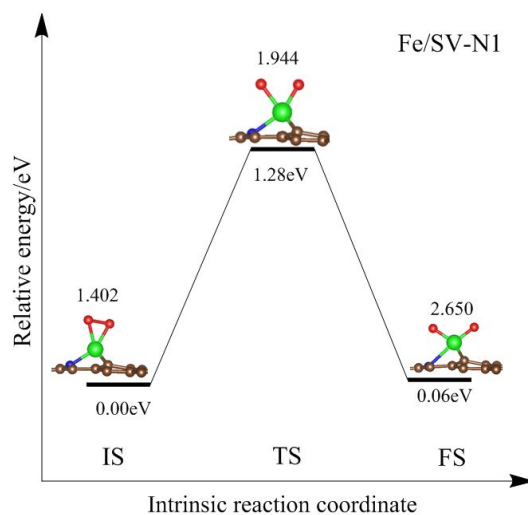
Fig. S2 The HOMO of Fe/GS

Table S3 The electronic structure characteristics analysis of Fe/GS

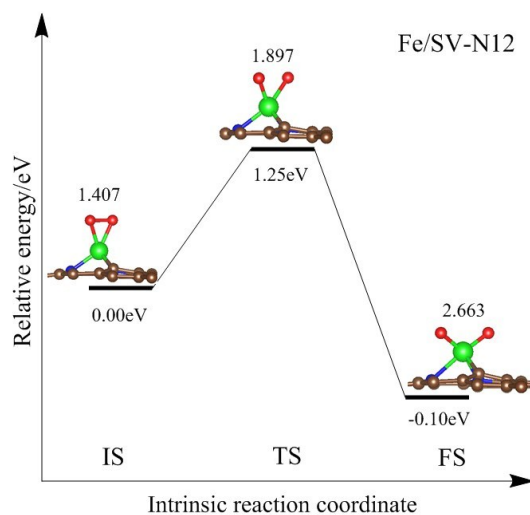
| Model          | $E_V/\text{eV}$ | $E_F/\text{eV}$ | $W/\text{eV}$ | $\Delta W/\text{eV}$ | $\Delta q/e$ | $E_{\text{ionic}}/\text{eV}$ | $S_F/\text{eV}$ | $E_{\text{ads}}/\text{eV}$ |
|----------------|-----------------|-----------------|---------------|----------------------|--------------|------------------------------|-----------------|----------------------------|
| O <sub>2</sub> | 0.03            | -6.72           | 6.75          | -                    | -            | -                            | -               | -                          |
| Fe/SV-GN       | 2.22            | -2.11           | 4.34          | -2.41                | 0.62         | -1.49                        | 5.72            | 1.99                       |
| Fe/SV-N1       | 2.16            | -1.85           | 4.02          | -2.73                | 0.68         | -1.85                        | 5.73            | 2.38                       |
| Fe/SV-N12      | 2.12            | -1.74           | 3.87          | -2.88                | 0.70         | -2.01                        | 5.80            | 3.04                       |
| Fe/SV-N123     | 2.21            | -1.71           | 3.91          | -2.83                | 0.75         | -2.11                        | 6.19            | 3.26                       |
| Fe/DV-GN       | 2.05            | -2.52           | 4.57          | -2.18                | 0.57         | -1.24                        | 5.67            | 1.85                       |
| Fe/DV-N1       | 1.99            | -2.47           | 4.46          | -2.29                | 0.57         | -1.31                        | 5.48            | 1.60                       |
| Fe/DV-N13      | 1.96            | -2.23           | 4.19          | -2.56                | 0.57         | -1.47                        | 5.37            | 1.81                       |
| Fe/DV-N14      | 1.95            | -2.45           | 4.39          | -2.35                | 0.56         | -1.32                        | 5.27            | 1.55                       |
| Fe/DV-N123     | 1.98            | -2.24           | 4.22          | -2.52                | 0.57         | -1.44                        | 5.15            | 1.19                       |
| Fe/DV-N1234    | 2.02            | -2.17           | 4.19          | -2.56                | 0.45         | -1.14                        | 5.26            | 0.76                       |



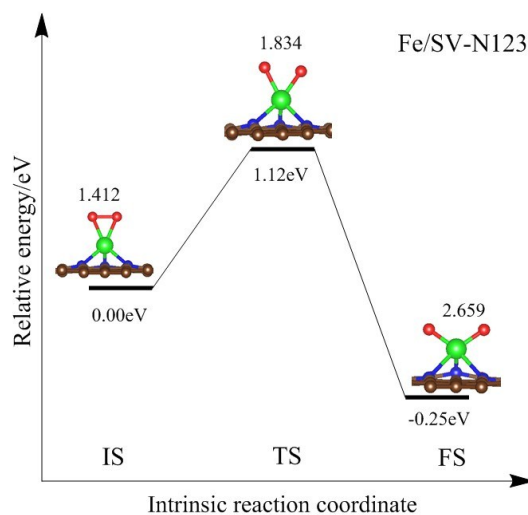
(a) Fe/SV-GN



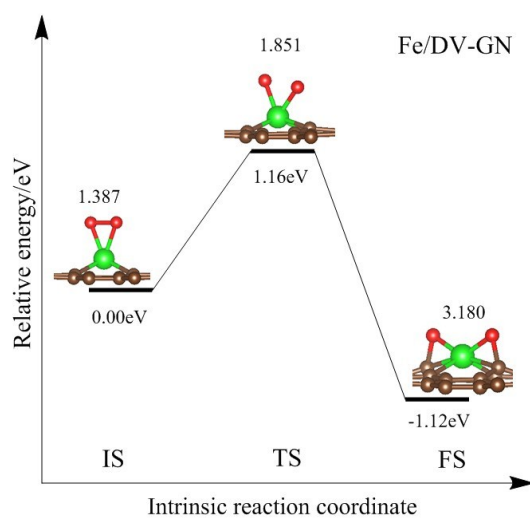
(b) Fe/SV-N1



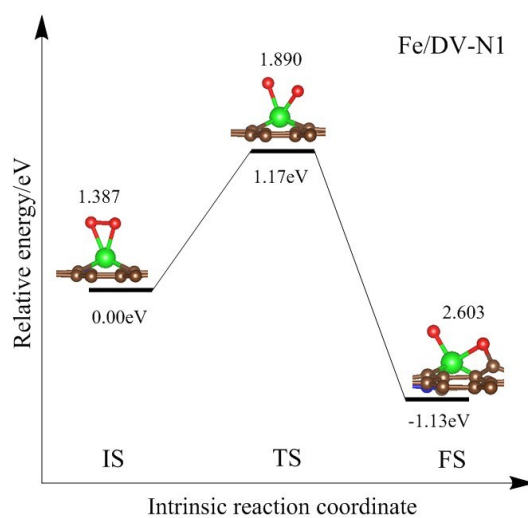
(b) Fe/SV-N12



(d) Fe/SV-N123



(e) Fe/DV-GN



(f) Fe/DV-N1

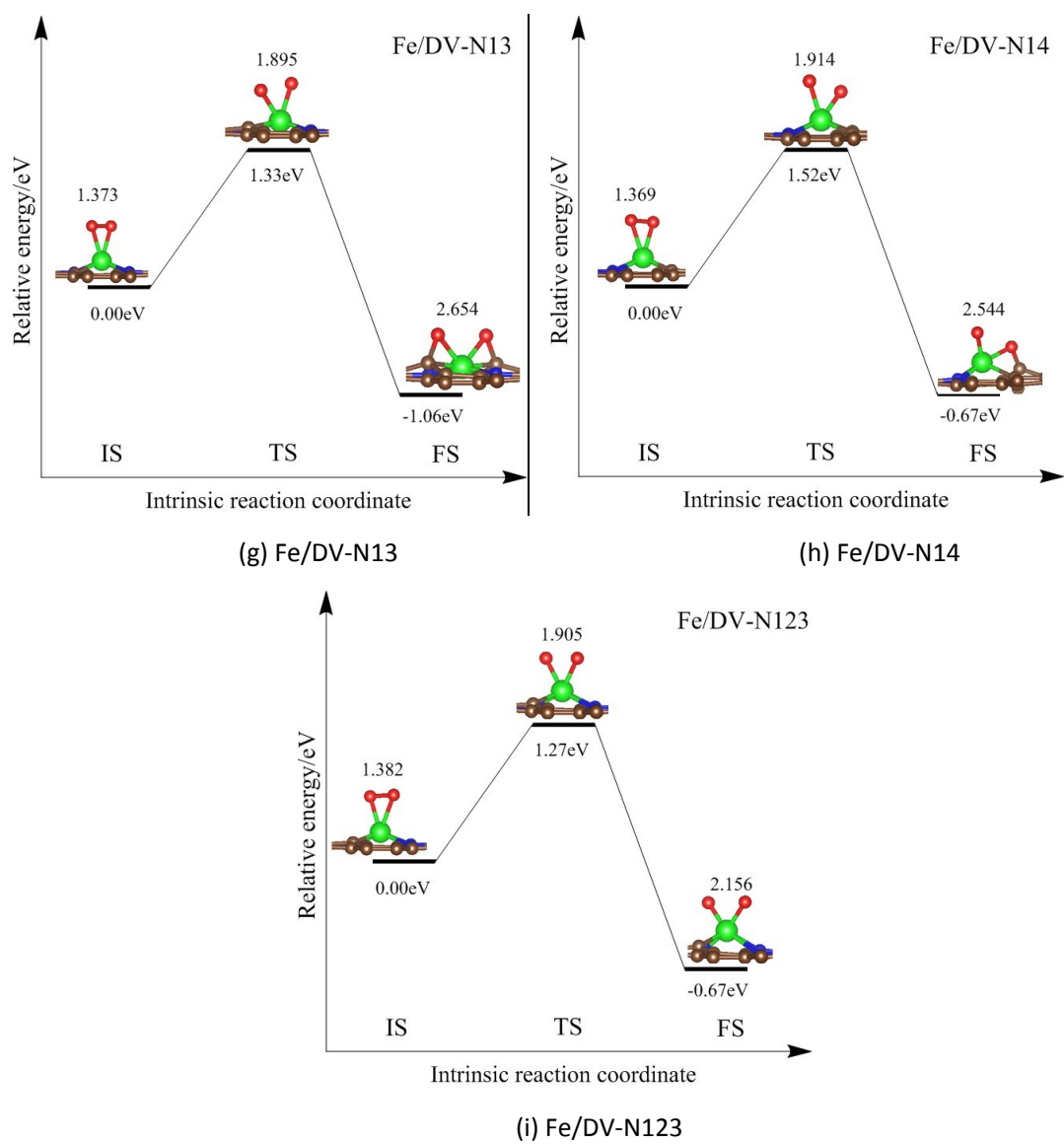


Fig. S3 The detailed reaction path of  $O_2$  dissociation on Fe/GS

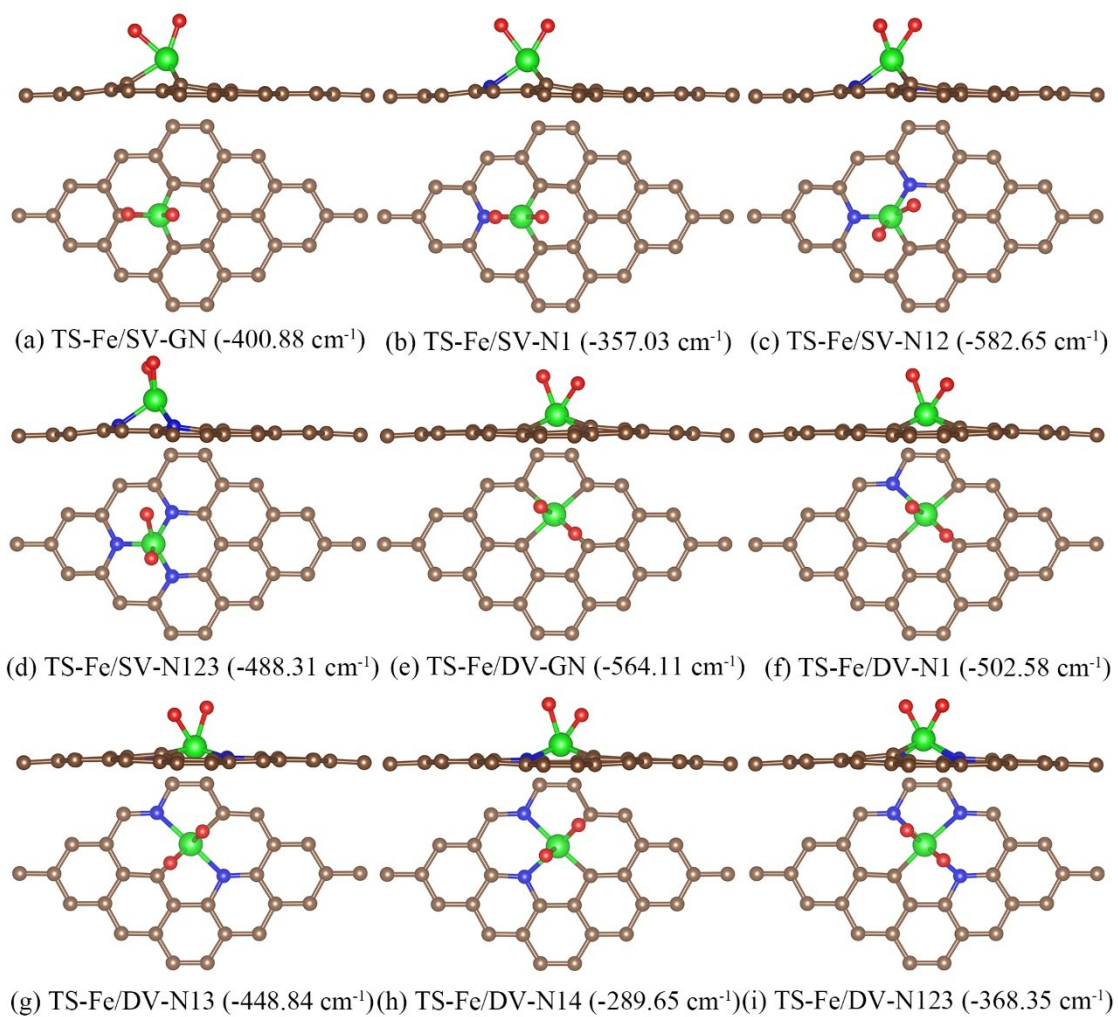


Fig. S4 The transition state structures of  $\text{O}_2$  on Fe/GS