Supporting Information

The geometrically optimized energies for the different structures constructed as shown in Fig. 2 are as follows.

Table S1. Detailed computational data for the binding energy of doped Fe on different active site structures

Type of site	E_1 (eV)	E_2 (eV)	E_{Fe} (eV)	$\triangle E = E_2 - E_1 - E_{Fe}$ (eV)	(kcal/mol)
a site					
a-1	-2,589.3793	-2,712.3029	-122.6962	-0.2274	-142.72
a-2	-2,589.3767	-2,712.3136	-122.6962	-0.2407	-151.07
a-3	-2,542.2346	-2,665.3629	-122.6962	-0.4321	-271.15
b site					
b-1	-2,955.4190	-3,078.3908	-122.6962	-0.2757	-173.01
b-2	-2,908.2844	-3,031.4145	-122.6962	-0.4339	-272.26

The energies and reaction intermediates for the direct catalytic decomposition of N_2O and the selective catalytic reduction reaction of N_2O by CO on the a-structure are given below.

Table S2. Energies of calculated results for reaction mechanisms on the a-structure.

Reaction	Number	State	Relative energy	Relative energy to the previous step
Part 1				
	A1	a+N_2O	0.00	
	A2	IM1-a-N_2O	-9.70	-9.70
	a-TS1	a-TS1	17.14	26.85
	A3	IM2-a-O*-N_2	-9.51	-26.65
	A4	a-O*+N_2	-6.11	3.39
Part 2-1				
	A5	IM3-a-O*-N_2O	-9.76	-3.65
	a-TS2-I	a-TS2-I	26.70	36.46
	A6	IM4-a-O*-O-N_2	-39.76	-66.46
	A7	a-O*-O+N_2	-39.09	0.67
	A8	a-O_2	-26.11	12.98
	A9	a+O_2	-37.97	-11.86
	A10	IM3-a-O*-N_2O	-9.60	-3.49
	a-TS2-II	a-TS2-II	40.11	49.71

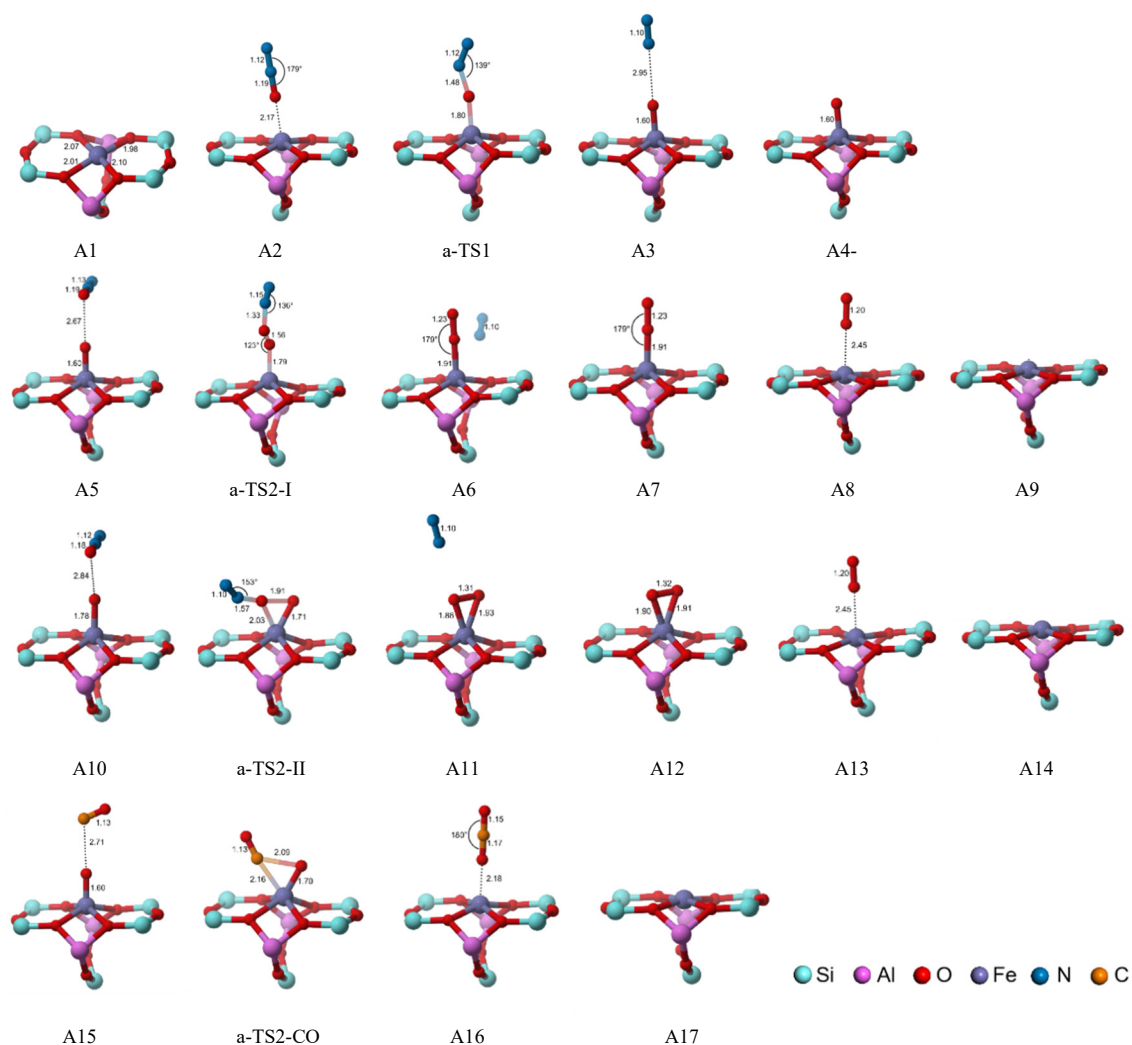|			
A11	IM4-a-O*-O-N$_2$	-28.33	-68.44
A12	a-O*-O+N$_2$	-25.66	2.67
A13	a-O$_2$	-26.04	-0.38
A14	a+O$_2$	-37.97	-11.92
Part 2-2			
A15	IM3-a-O*-CO	-9.17	-3.06
a-TS2-CO	a-TS2-CO	6.72	15.89
A16	IM4-a-CO$_2$	-96.74	-103.46
A17	a+CO$_2$	-86.67	10.07

Figure S1. Reaction intermediates and transition states calculated by reaction mechanism on the a-structure (the unit of bond length is Å)

The energies and reaction intermediates for the direct catalytic decomposition of N_2O and the selective catalytic reduction reaction of N_2O by CO on the b-structure are given below.

Table S3. Energies of calculated results for reaction mechanisms on the b-structures.

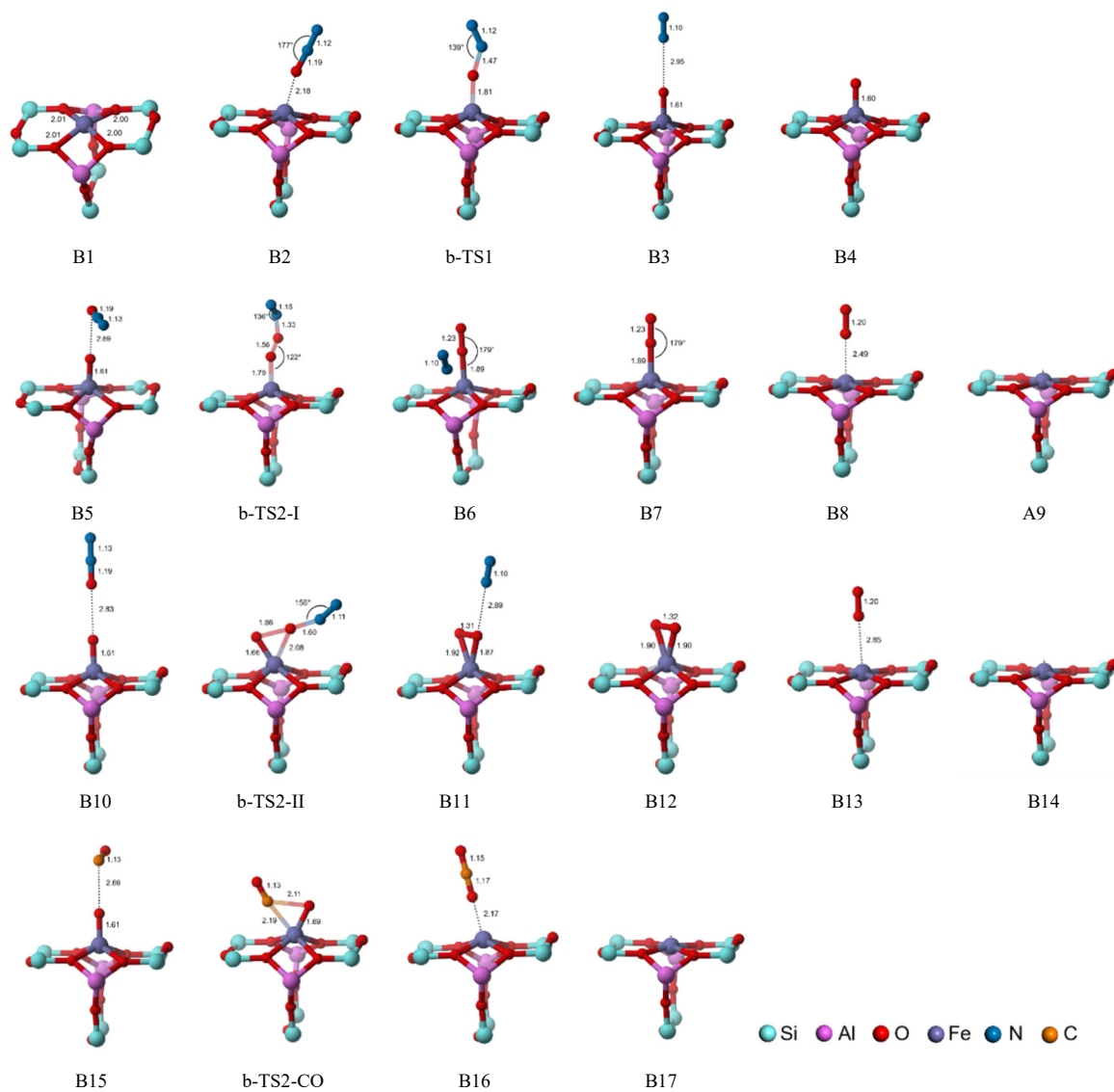| Reaction	Number	State	Relative energy	Relative energy to the previous step
Part 1				
		TS1		
	B1	$b+N_2O$	0.00	
	B2	$IM1-b-N_2O$	-11.64	-11.64
	b-TS1	b-TS1	12.72	24.36
	B3	$IM2-b-O^*-N_2$	-13.09	-25.81
	B4	$b-O^*+N_2$	-9.80	3.29
Part 2-1				
		TS2-I		
	B5	$IM3-b-O^*-N_2O$	-16.51	-6.71
	b-TS2-I	b-TS2-I	18.95	35.46
	B6	$IM4-b-O^*-O-N_2$	-45.98	-64.93
	B7	$b-O^*-O+N_2$	-45.06	0.92
	B8	$b-O_2$	-32.68	12.38
	B9	$b+O_2$	-44.39	-11.71
		TS2-II		
	B10	$IM3-b-O^*-N_2O$	-16.81	-7.01
	b-TS2-II	b-TS2-II	34.04	50.86
	B11	$IM4-b-O^*-O-N_2$	-36.35	-70.40
	B12	$b-O^*-O+N_2$	-33.54	2.81
	B13	$b-O_2$	-32.91	0.63
	B14	$b+O_2$	-44.39	-11.48
Part 2-2				
		TS2-CO		
	B15	$IM3-b-O^*-CO$	-12.74	-2.94
	b-TS2-CO	b-TS2-CO	3.23	15.97
	B16	$IM4-b-CO_2$	-98.81	-102.04
	B17	$b+CO_2$	-89.88	8.93

Figure S2. Reaction intermediates and transition states calculated by reaction mechanism on the b-structure(the unit of bond length is Å)

The atomic charge distribution of certain structures during reaction progress has been determined as follows.

Table S4. Charge distribution of N_2O and CO molecules

Molecule	Atom		
	O	N	N
N_2O	-0.1493	0.2335	-0.0842
	C	O	/
CO	0.0841	-0.0841	/

Table S5. Charge distribution of reaction intermediates and transition states for N_2O decomposition

over Z(Fe) of the a-structure

Number	Process	State	Atom			
			Fe	O	N	N
1		a	0.4446	/	/	/
2	TS1	a-N_2O	0.3771	-0.0556	0.2725	-0.0126
3		a-N_2O-TS	0.4959	-0.1981	0.1474	0.0162
4		a-O*-N_2	0.5028	-0.1716	0.0119	-0.0014

The results of the computational tests with and without BSSE corrections of the a-structure are as follows

Table S6. Partial interaction energies with and without BSSE correction of the a-structure

Number	State	Interaction energy (kcal/mol)	
		Without BSSE	With BSSE
A2	N_2O adsorption	-9.7	0.92
A3	N_2 desorption	3.39	-0.53
A5	N_2O adsorption	-3.65	0.41
A6	N_2 desorption	0.67	-0.45
A8	O_2 desorption	-11.86	-14.98
A10	N_2O adsorption	-3.49	0.24
A11	N_2 desorption	2.67	-0.74
A13	O_2 desorption	-11.92	-8.89
A15	CO_2 adsorption	-3.06	0.32
A16	CO_2 desorption	10.07	8.03