Supporting information for "Theoretical insights into alkaline metal M (M=Na and Cs) promotion mechanism for CO_2 activation on the Cu (111) surface"

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1. The geometry structures of CO_2 on clean and Na and Cs-promoted Cu(111)

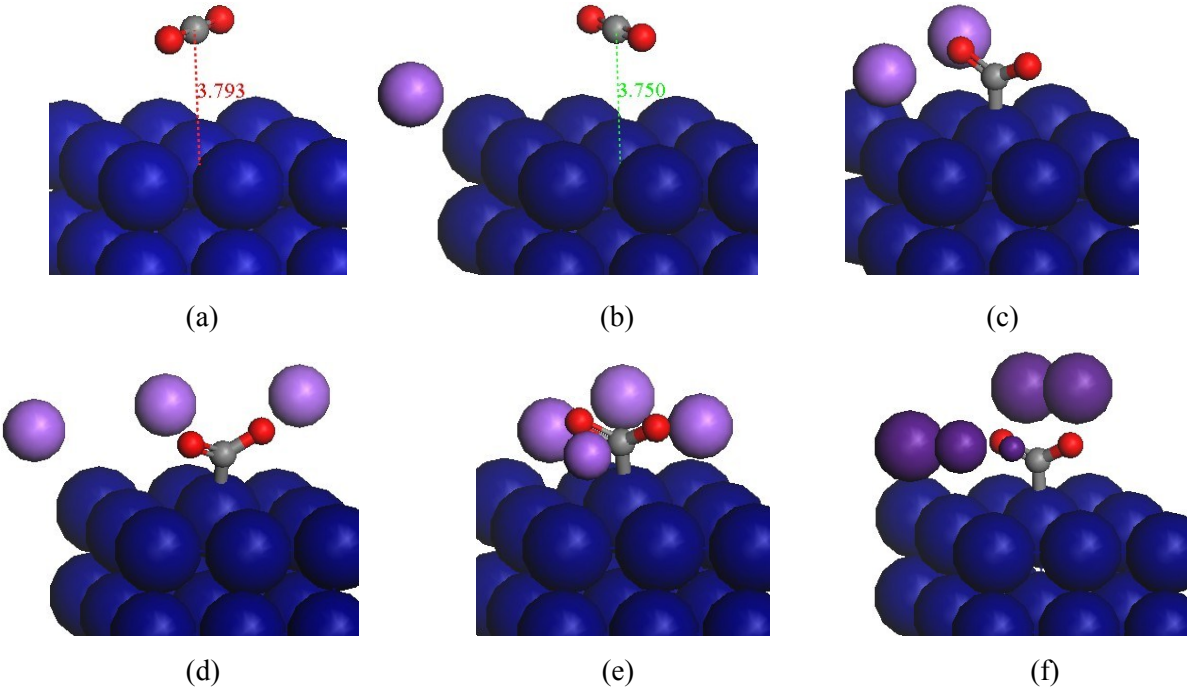
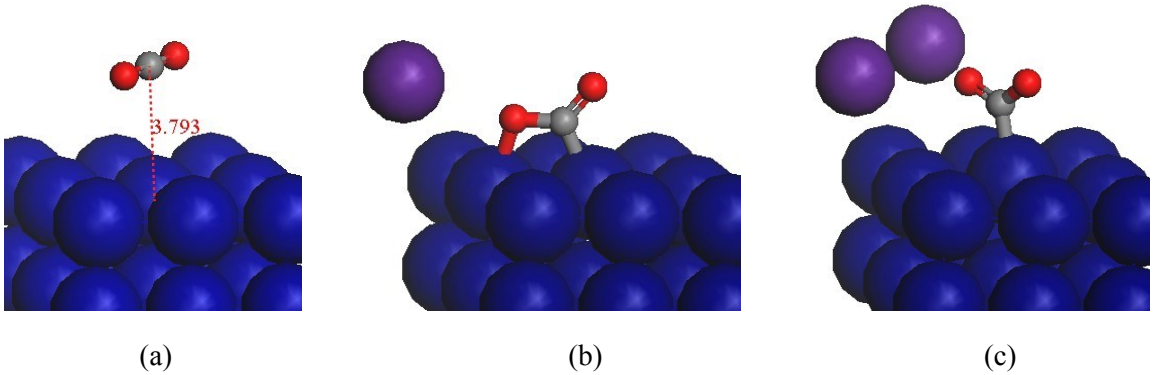


Fig. S1 The optimized geometry structures of CO_2 on clean and alkaline metals Na-promoted Cu(111) surface: (a) Clean; (b) 1/9 Na; (c) 2/9 Na; (d) 3/9 Na; (e) 4/9 Na; (f) 5/9 Na.



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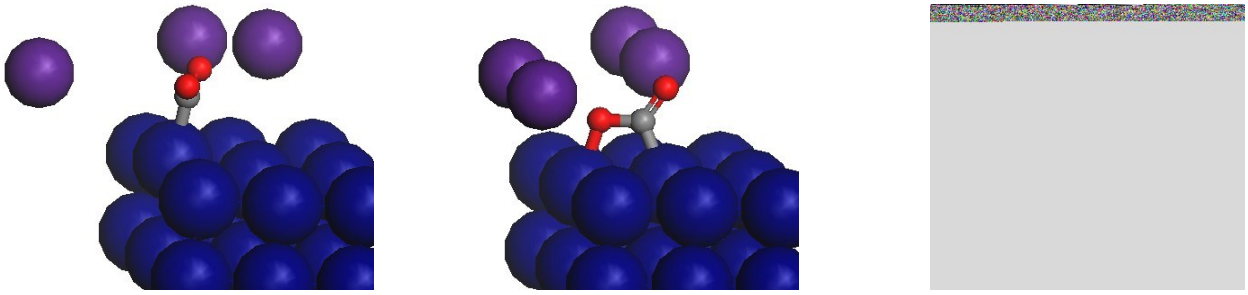

(d) (e) (f)

Fig. S2 The optimized geometry structures of CO_2 on clean and alkaline metals Cs-promoted Cu(111) surface: (a) Clean; (b) 1/9 Cs; (c) 2/9 Cs; (d) 3/9 Cs; (e) 4/9 Cs; (f) 5/9 Cs.

2. Computational details on work function

The work function was calculated. By definition, the work function W is the minimum energy required to extract one electron from the surface to an infinite distance, which can be best calculated in the framework of DFT nowadays.[1, 2] The work function is dependent sensitively on the surface ionic and electronic charge distributions, and any surface atomic relaxation or reconstruction may be able to influenced it. Thus, these calculations present a theoretical challenge. Generally, making use of slab configurations to calculate surface properties is the most efficient first-principles methods at present. The expression of work function calculation is exactly equivalent to:[3] $W = V_{vacuum} - E_F$, where V_{vacuum} is vacuum level, and it is defined to be mean electrostatic potential perpendicular to vacuum layer, E_F is the Fermi level of system. The PROPROCESSING and AVERAGE codes contained in the Quantum ESPRESSO distribution were used to calculate V_{vacuum}. The electrostatic potential is first obtained for the present systems, and then the macroscopic averages of electrostatic potential for various states are evaluated. For example, on clean Cu(111), V_{vacuum} is evaluated from the slab by means of the macroscopic average of the total electrostatic potential, if vacuum layer is thick enough, one should find a constant value in the vacuum layer region. This value, we then can refer to vacuum level, and the position of the Fermi level E_F is also evaluated by Cu slab configurations (see Fig. S3).

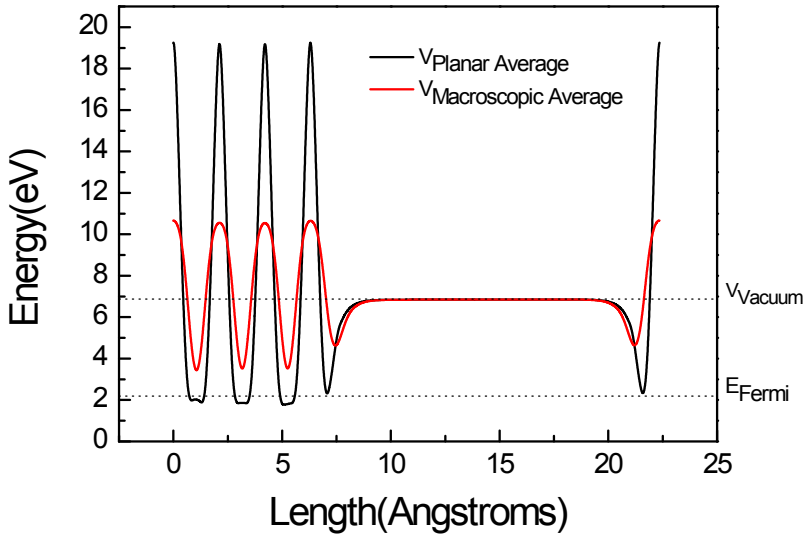

Fig. S3 Planar averaged total electrostatic potential (black line) and corresponding macroscopic average (red line) for clean Cu(111) surface. The vacuum level V_{vacuum} and the slab Fermi level E_F are indicated.

Table S1 The calculated vacuum level, V_{vacuum} and Fermi level, E_{Fermi} for the clean Cu(111) and Na and Cs-promoted Cu(111) in the absence of CO_2 molecule on the Cu (111) surface

Alkaline Metal	V_{vacuum} (eV)	E_{Fermi}	Alkaline Metal	V_{vacuum} (eV)	E_{Fermi}
0	6.87	2.19	0	6.87	2.19
1/9 Na	7.40	2.92	1/9 Cs	7.66	3.30
2/9 Na	7.73	3.22	2/9 Cs	8.00	3.52
3/9 Na	8.00	3.43	3/9 Cs	8.02	3.59
4/9 Na	8.00	3.51	4/9 Cs	8.02	3.66
5/9 Na	8.00	3.52	5/9 Cs	8.12	3.76

3. Computational details on Löwdin population analysis

The Löwdin population analyses are carried out in the present study. Based on the projected electron densities of states, the Löwdin charge (the number of valence electron) of each surface with different Na and Cs coverage can be obtained from Löwdin population analysis in the absence and presence of CO_2. Tables S2 and S3 gives the average electron gains (Δq) for surface Cu, Na and Cs atoms in Na and Cs-promoted Cu(111) in the absence of CO_2, respectively, Tables S4 and S5 give the average electron gains (Δq) for CO_2, surface Cu, Na and Cs atoms in Na and Cs-promoted Cu(111) in the presence of CO_2, respectively, which were obtained by subtracting the Löwdin charge of the corresponding component of clean Cu(111) surface and isolated Na and Cs atoms from that in the optimized structure. A gain of electron by the component will be implied by a positive value of Δq.

Table S2 The average electron gains (Δq) of total, *s*, *p*, and *d* orbitals of surface Cu and Na atoms in Na-promoted Cu(111) in the absence of CO_2 compared to clean Cu(111) surface and isolated Na atoms

		Difference of Average Electron/Atom (Δq)			
		Total	*s*	*p*	*d*
Isolated	Cu	0.0000	0.0000	/	0.0000
	Na	0.0000	0.0000	0.0000	/
1/9 Na	Cu	+0.0314	+0.0289	/	+0.0023
	Na	-0.4414	-0.4413	-0.0002	/
2/9 Na	Cu	+0.0338	+0.0324	/	+0.0013
	Na	-0.2505	-0.2501	-0.0005	/
3/9 Na	Cu	+0.0398	+0.0374	/	+0.0023
	Na	-0.1549	-0.1547	-0.0003	/
4/9 Na	Cu	+0.0489	+0.0479	/	+0.0010
	Na	-0.1210	-0.1205	-0.0006	/
5/9 Na	Cu	+0.0548	+0.0530	/	+0.0016
	Na	-0.1168	-0.1155	-0.0013	/

Table S3 The average electron gains (Δq) of total, *s*, *p*, and *d* orbitals of surface Cu and Cs atoms in Cs-promoted Cu(111) in the absence of CO_2 compared to clean Cu(111) surface and isolated Cs atoms

		Difference of Average Electron/Atom (Δq)			
		Total	*s*	*p*	*d*
Isolated	Cu	0.0000	0.0000	/	0.0000
	Cs	0.0000	0.0000	0.0000	0.0000
1/9 Cs	Cu	-0.0389	-0.0280	/	-0.0110
	Cs	+0.4192	-0.0065	+0.0709	+0.4129
2/9 Cs	Cu	-0.1215	-0.0951	/	-0.0265
	Cs	+0.6265	+0.0036	+0.0509	+0.5719
3/9 Cs	Cu	-0.1731	-0.1431	/	-0.0301
	Cs	+0.6399	-0.0884	+0.0013	+0.7270
4/9 Cs	Cu	-0.1444	-0.1167	/	-0.0278
	Cs	+0.4179	-0.2569	-0.1248	+0.7995
5/9 Cs	Cu	-0.1617	-0.1324	/	-0.0294
	Cs	+0.3521	-0.2948	-0.1309	+0.7778

Table S4 The average electron gains (Δq) of total, *s*, *p*, and *d* orbitals of CO_2, surface Cu and Na atoms in Na-promoted Cu(111) in the presence of CO_2 compared to clean Cu(111) surface and isolated CO_2 and Na atoms

		Difference of Average Electron/Atom (Δq)			
		Total	*s*	*p*	*d*
Isolated	Cu	0.0000	0.0000	/	0.0000
	Na	0.0000	0.0000	0.0000	/
	C	0.0000	0.0000	0.0000	/
	O	0.0000	0.0000	0.0000	/
	O	0.0000	0.0000	0.0000	/
0 Na	Cu	+0.0008	+0.0007	/	0.0000
	C	+0.0101	+0.0028	+0.0072	/
	O	+0.0011	0.0000	+0.0011	/
	O	+0.0011	-0.0001	+0.0011	/
1/9 Na	Cu	+0.0351	+0.0328	/	+0.0020
	Na	-0.4806	-0.4804	-0.0003	/
	C	-0.0145	+0.0014	-0.0159	/
	O	+0.0428	-0.0172	+0.0601	/
	O	-0.0306	-0.0046	-0.0206	/
2/9 Na	Cu	+0.0067	+0.0177	/	-0.0112
	Na	-0.5535	-0.5531	-0.0005	/
	C	+0.4842	+0.2960	+0.1882	/
	O	+0.1754	+0.0317	+0.1437	/
	O	+0.3508	+0.0387	+0.3121	/
3/9 Na	Cu	+0.0140	+0.0249	/	-0.0110
	Na	-0.4882	-0.4876	-0.0007	/
	C	+0.6151	+0.3807	+0.2344	/
	O	+0.3280	+0.0420	+0.2860	/
	O	+0.3454	+0.0485	+0.2969	/
4/9 Na	Cu	+0.0171	+0.0262	/	-0.0091
	Na	-0.3843	-0.3832	-0.0012	/
	C	+0.6771	+0.4065	+0.2706	/
	O	+0.3924	+0.0500	+0.3424	/
	O	+0.3235	+0.0426	+0.2809	/
5/9 Na	Cu	+0.0248	+0.0337	/	-0.0090
	Na	-0.3435	-0.3427	-0.0009	/
	C	+0.6832	+0.4427	+0.2404	/
	O	+0.3917	+0.0544	+0.3372	/
	O	+0.3934	+0.0547	+0.3387	/

Table S5 The average electron gains (Δq) of total, *s*, *p*, and *d* orbitals of CO_2, surface Cu and Cs atoms in Cs-promoted Cu(111) in the presence of CO_2 compared to clean Cu(111) surface and isolated CO_2 and Cs atoms

		Difference of Average Electron/Atom (Δq)			
		Total	*s*	*p*	*d*
Isolated	Cu	0.0000	0.0000	/	0.0000
	Cs	0.0000	0.0000	0.0000	0.0000
	C	0.0000	0.0000	0.0000	/
	O	0.0000	0.0000	0.0000	/
	O	0.0000	0.0000	0.0000	/
0 Cs	Cu	+0.0008	+0.0007	/	0.0000
	C	+0.0101	+0.0028	+0.0072	/
	O	+0.0011	0.0000	+0.0011	/
	O	+0.0011	-0.0001	+0.0011	/
1/9 Cs	Cu	-0.0706	-0.0477	/	-0.0230
	Cs	+0.1488	-0.2459	+0.0371	+0.3577
	C	+0.4625	+0.2575	+0.2050	/
	O	+0.0584	-0.0162	+0.0745	/
	O	+0.1895	+0.0180	+0.1714	/
2/9 Cs	Cu	-0.1117	-0.0861	/	-0.0257
	Cs	+0.3313	-0.1973	+0.0510	+0.4775
	C	+0.4623	+0.2591	+0.2032	/
	O	+0.1056	-0.0320	+0.1377	/
	O	+0.1041	-0.0323	+0.1364	/
3/9 Cs	Cu	-0.1756	-0.1393	/	-0.0364
	Cs	+0.4354	-0.2093	+0.0111	+0.6336
	C	+0.4798	+0.2764	+0.2034	/
	O	+0.1005	-0.0294	+0.1300	/
	O	+0.0950	-0.0360	+0.1310	/
4/9 Cs	Cu	-0.1570	-0.1202	/	-0.0370
	Cs	+0.1640	-0.3371	-0.0101	+0.6024
	C	+0.4755	+0.2545	+0.2210	/
	O	+0.0173	-0.0493	+0.0666	/
	O	+0.1464	-0.0047	+0.1511	/
5/9 Cs	Cu	-0.1573	-0.1219	/	-0.0355
	Cs	+0.2225	-0.3502	-0.1287	+0.7014
	C	+0.4064	+0.1949	+0.2115	/
	O	+0.0303	-0.0432	+0.0734	/
	O	+0.0319	-0.0435	+0.0754	/

References

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2 H. L. Skriver and N. M. Rosengaard, *Phys. Rev. B*, 1992, **46**, 7157−7168.

3 N. D. Lang and W. Kohn, *Phys. Rev. B*, 1971, **3**, 1215−1222.