

Unveiling the origin of alkali metal(Na, K, Rb, and Cs) promotion in CO₂ dissociation over Mo₂C catalysts

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Table S1 The key structural parameters of Mo₂C and X-Mo₂C

Catalysts	Bond lengths/Å
Mo ₂ C	Mo ₁ -Mo ₃ 3.14, Mo ₁ -Mo ₄ 2.88, Mo ₃ -Mo ₄ 3.09
Na-Mo ₂ C	Na-Mo ₁ 3.27, Na-Mo ₃ 3.22, Na-Mo ₄ 3.30, Mo ₁ -Mo ₃ 3.18, Mo ₁ -Mo ₄ 2.85, Mo ₃ -Mo ₄ 3.14
K-Mo ₂ C	K-Mo ₁ 3.84, K-Mo ₃ 3.58, K-Mo ₄ 3.75, Mo ₁ -Mo ₃ 3.18, Mo ₁ -Mo ₄ 2.85, Mo ₃ -Mo ₄ 3.15
Rb-Mo ₂ C	Rb-Mo ₁ 4.02, Rb-Mo ₃ 3.74, Rb-Mo ₄ 3.94, Mo ₁ -Mo ₃ 3.18, Mo ₁ -Mo ₄ 2.85, Mo ₃ -Mo ₄ 3.15
Cs-Mo ₂ C	Cs-Mo ₁ 4.16, Cs-Mo ₃ 3.87, Cs-Mo ₄ 4.09, Mo ₁ -Mo ₃ 3.18, Mo ₁ -Mo ₄ 2.86, Mo ₃ -Mo ₄ 3.14

Table S2 Adsorption energies (Kcal/mol) and bond length (Å) of all possible intermediates on the X(Na,K,Rb,Cs)-Mo₂C catalysts

	Species	E _{ads} (Kcal/mol)	Bond length(Å)
Mo ₂ C	CO ₂	-30.83	C-Mo ₃ 2.24, C-Mo ₃ 2.24, O _a - Mo ₃ 2.12, O _b -Mo ₅ 2.43, C-O _a 1.26, C-O _b 1.26,
	CO	-53.69	C-Mo ₄ 2.27, C-Mo ₅ 1.99, O-Mo ₄ 2.35, C-O 1.23
	O	-80.74	O-Mo ₃ 2.10, O-Mo ₄ 2.09, O-Mo ₅ 2.04
Na-Mo ₂ C	CO ₂	-41.17	C-Mo ₅ 2.17, O _a -Mo ₃ 2.13, O _b -Mo ₄ 2.12, C-O _a 1.35, C-O _b 1.35, Na-O _a 2.41, Na-O _b 2.41
	CO	-55.44	C-Mo ₃ 2.39, C-Mo ₅ 2.00, O-Mo ₃ 2.93, C-O 1.22, Na-O 2.42
	O	-81.84	O-Mo ₃ 2.15, O-Mo ₄ 2.15, O-Mo ₅ 2.06, Na-O 2.39
K-Mo ₂ C	CO ₂	-38.74	C-Mo ₅ 2.17, O _a -Mo ₃ 2.13, O _b -Mo ₄ 2.12, C-O _a 1.35, C-O _b 1.35, K-O _a 2.74, K-O _b 2.97
	CO	-56.36	C-Mo ₄ 2.26, C-Mo ₅ 1.98, O-Mo ₄ 2.40, C-O 1.25, K-O 2.78
	O	-82.10	O-Mo ₃ 2.14, O-Mo ₄ 2.13, O-Mo ₅ 2.06, K-O 2.85
Rb-Mo ₂ C	CO ₂	-38.02	C-Mo ₅ 2.19, O _a -Mo ₃ 2.13, O _b -Mo ₄ 2.09, C-O _a 1.34, C-O _b 1.36, Rb-O _a 3.08, Rb-O _b 2.96
	CO	-55.61	C-Mo ₃ 2.42, C-Mo ₅ 2.00, O-Mo ₃ 3.04, C-O 1.25, Rb-O 2.93
	O	-81.95	O-Mo ₃ 2.13, O-Mo ₄ 2.13, O-Mo ₅ 2.06, Rb-O 3.03
Cs-Mo ₂ C	CO ₂	-38.17	C-Mo ₅ 2.16, O _a -Mo ₃ 2.17, O _b -Mo ₄ 2.09, C-O _a 1.33, C-O _b 1.36, Cs-O _a 3.06, Cs-O _b 3.16
	CO	-55.97	C-Mo ₃ 2.42, C-Mo ₅ 2.01, O-Mo ₃ 3.04, C-O 1.21, Cs-O 3.18
	O	-81.81	O-Mo ₃ 2.14, O-Mo ₄ 2.13, O-Mo ₅ 2.06, Cs-O 3.04

Table S3 Mulliken charge(e) of CO₂*-X-Mo₂C

Atom	Mo ₂ C	Na-Mo ₂ C	K-Mo ₂ C	Rb-Mo ₂ C	Cs-Mo ₂ C
Mo ₁	0.08	-0.12	-0.11	-0.07	-0.08
Mo ₂	0.16	0.11	0.11	0.17	0.14
Mo ₃	0.10	0.17	0.17	0.22	0.20
Mo ₄	0.10	0.09	0.08	0.11	0.09
Mo ₅	0.10	0.10	0.11	0.14	0.12
Mo ₆	0.13	0.09	0.12	0.15	0.15
O _a	-0.36	-0.52	-0.51	-0.51	-0.49
C	0.43	0.30	0.31	0.25	0.32
O _b	-0.36	-0.52	-0.51	-0.48	-0.52
Alkali metal	/	0.72	0.82	0.76	0.74

Table S4 Mulliken charge(e) of CO*-X-Mo₂C

Atom	Mo ₂ C	Na-Mo ₂ C	K-Mo ₂ C	Rb-Mo ₂ C	Cs-Mo ₂ C
Mo ₁	0.04	-0.08	-0.09	-0.04	-0.04
Mo ₂	0.14	0.09	0.10	0.13	0.12
Mo ₃	0.18	0.08	0.07	0.20	0.18
Mo ₄	0.09	-0.04	-0.02	-0.05	-0.05
Mo ₅	0.08	0.03	0.07	0.10	0.06
Mo ₆	0.20	0.10	0.16	0.14	0.12
O	-0.28	-0.33	-0.40	-0.31	-0.31
C	0.04	0.08	0.00	-0.02	0.02
Alkali metal	/	0.65	0.80	0.73	0.76

Table S5 Mulliken charge(e) of O*-X-Mo₂C

Atom	Mo ₂ C	Na-Mo ₂ C	K-Mo ₂ C	Rb-Mo ₂ C	Cs-Mo ₂ C
Mo ₁	0.06	-0.09	-0.10	-0.07	-0.07
Mo ₂	0.13	0.09	0.09	0.13	0.12
Mo ₃	0.30	0.18	0.20	0.25	0.24
Mo ₄	0.27	0.15	0.15	0.17	0.16
Mo ₅	0.32	0.26	0.27	0.30	0.28
O	-0.66	-0.74	-0.73	-0.72	-0.73
Alkali metal	/	0.67	0.79	0.72	0.73