Supplementary information

A predicted new catalyst to replace noble metal Pd for CO oxidative coupling to DMO

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The adsorption energy of related species in the CO oxidative coupling to DMO is calculated by the following formula (1):

$$E_{\text{ads}} = E_{\text{catalyst}} + E_{\text{adsorbate}} - E_{\text{total}} \tag{1}$$

where the E_{total}, E_{catalyst} and $E_{\text{adsorbate}}$ represent the energies of the system after adsorption, catalyst and the adsorption species in the gas state, respectively.

The activation energy for the elementary reaction is defined as formula (2):

$$E_{\text{a}} = E_{\text{TS}} - E_{\text{R}} \tag{2}$$

where E_{TS} and E_{R} represent the energies of transition state and initial reactant. The heat of reaction (ΔH) is the difference in energy between the products and the reactants in each step of the elementary reaction.

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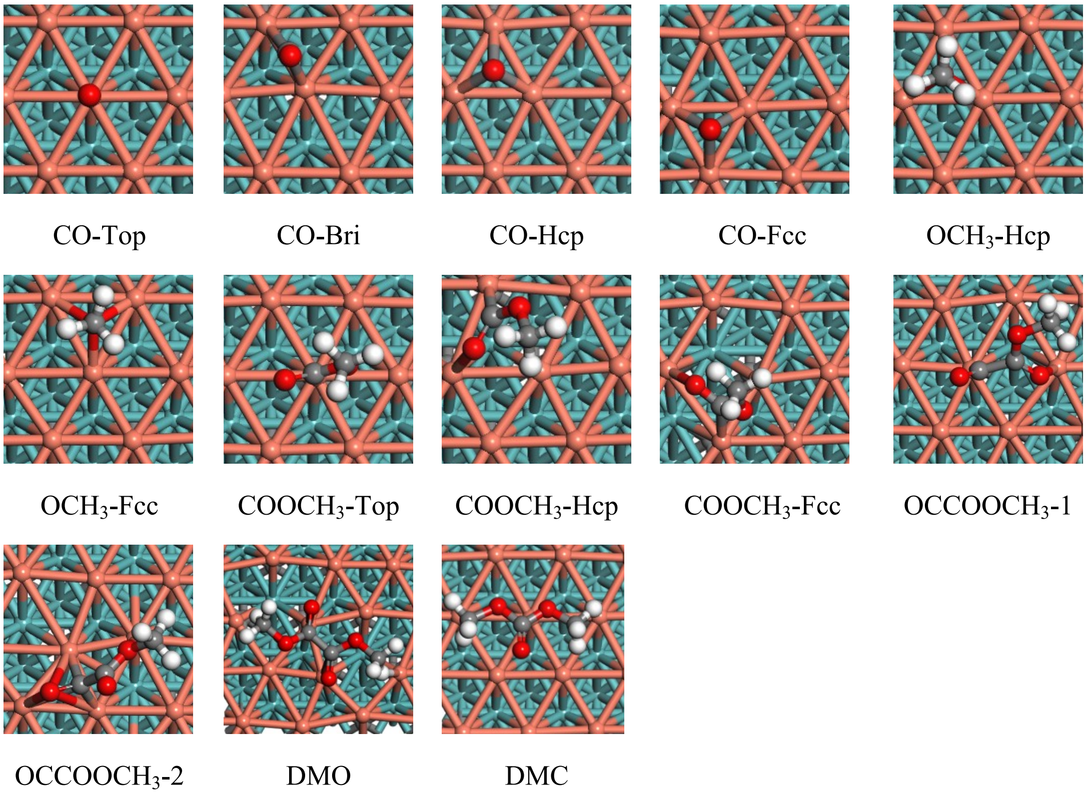


CO-Top
CO-Bri
CO-Hcp
CO-Fcc
OCH_3-Hcp
OCH_3-Fcc
$COOCH_3$-Top
$COOCH_3$-Hcp
$COOCH_3$-Fcc
$OCCOOCH_3$-1
$OCCOOCH_3$-2
DMO
DMC

Fig. S1 The stable adsorption configurations of all possible species involved in CO oxidative coupling to DMO on $Cu_{ML}/Mo_2C(001)$-Mo

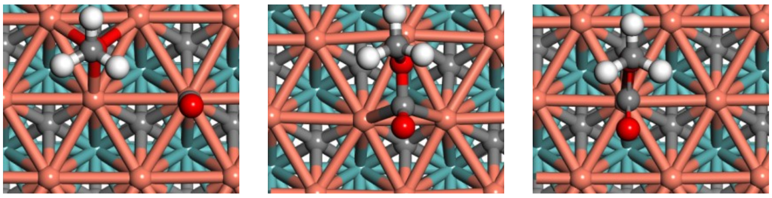
Table S1. Frequency analysis results with different convergence thresholds aiming at the elementary step of CO + OCH_3 → $COOCH_3$, where R represents the co-adsorption reactant structure of CO and OCH_3, and TS represents the structure of the transition state.

		3×10^{-2} eV/Å	1×10^{-3} eV/Å
R	1f=	3023.551287 cm^{-1}	3023.823061 cm^{-1}
	2f=	3018.405931 cm^{-1}	3018.640689 cm^{-1}
	3f=	2938.36268 cm^{-1}	2939.90559 cm^{-1}
	4f=	1859.102083 cm^{-1}	1859.106077 cm^{-1}
	5f=	1439.596192 cm^{-1}	1439.694175 cm^{-1}
	6f=	1433.469328 cm^{-1}	1433.59131 cm^{-1}
	7f=	1408.901027 cm^{-1}	1409.20976 cm^{-1}
	8f=	1125.765208 cm^{-1}	1125.778408 cm^{-1}
	9f=	1123.203483 cm^{-1}	1123.71934 cm^{-1}
	10f=	1012.580466 cm^{-1}	1012.618528 cm^{-1}
	11f=	304.356177 cm^{-1}	304.406351 cm^{-1}
	12f=	279.084195 cm^{-1}	279.512533 cm^{-1}
	13f=	263.231014 cm^{-1}	263.086542 cm^{-1}
	14f=	254.263831 cm^{-1}	254.089123 cm^{-1}
	15f=	248.220018 cm^{-1}	248.185307 cm^{-1}
	16f=	238.191636 cm^{-1}	238.791594 cm^{-1}
	17f=	147.736505 cm^{-1}	146.857294 cm^{-1}
	18f=	117.626112 cm^{-1}	118.192632 cm^{-1}
	19f=	96.265582 cm^{-1}	101.558081 cm^{-1}
	20f=	71.604103 cm^{-1}	70.58699 cm^{-1}
	21f=	64.888047 cm^{-1}	65.599333 cm^{-1}
TS	1f=	3072.794289 cm^{-1}	3072.980233 cm^{-1}
	2f=	3066.24665 cm^{-1}	3066.40928 cm^{-1}
	3f=	2974.821356 cm^{-1}	2975.265489 cm^{-1}

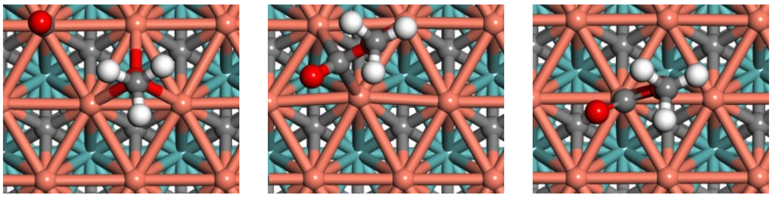
4f=	1853.30005 cm^{-1}	1853.324602 cm^{-1}
5f=	1439.499124 cm^{-1}	1439.558381 cm^{-1}
6f=	1418.745541 cm^{-1}	1418.781361 cm^{-1}
7f=	1389.230652 cm^{-1}	1389.65779 cm^{-1}
8f=	1120.127671 cm^{-1}	1120.314964 cm^{-1}
9f=	1117.006869 cm^{-1}	1117.175952 cm^{-1}
10f=	944.612626 cm^{-1}	944.900619 cm^{-1}
11f=	675.23722 cm^{-1}	675.194916 cm^{-1}
12f=	451.623252 cm^{-1}	451.67706 cm^{-1}
13f=	290.782046 cm^{-1}	290.472065 cm^{-1}
14f=	263.789998 cm^{-1}	263.473065 cm^{-1}
15f=	236.967577 cm^{-1}	236.039743 cm^{-1}
16f=	209.434889 cm^{-1}	209.943035 cm^{-1}
17f=	136.75103 cm^{-1}	135.884992 cm^{-1}
18f=	70.78665 cm^{-1}	70.483487 cm^{-1}
19f=	64.034015 cm^{-1}	65.075324 cm^{-1}
20f=	39.769348 cm^{-1}	42.422764 cm^{-1}
21f/i=	121.739269 cm^{-1}	121.30625 cm^{-1}

Table S2. Adsorption sites and adsorption energies of some possible species involved in CO oxidative coupling to DMO on $Cu_{ML}/Mo_2C(001)$-Mo (kJ/mol)

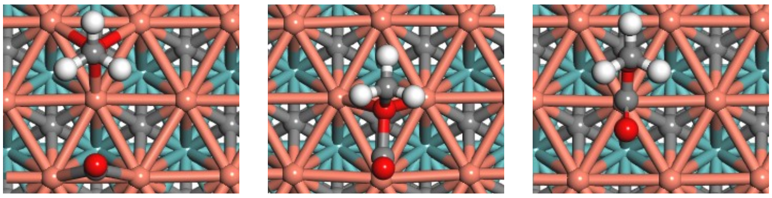
	$Cu_{ML}/Mo_2C(001)$-Mo			
	Top	Bri	Hcp	Fcc
CO	111.6	111.3	107.4	116.2
OCH_3	-	-	268.5	294.8
$COOCH_3$	185.0	-	214.6	226.8
$OCCOOCH_3$	182.2	187.2		
DMO	30.5			
DMC	6.6			



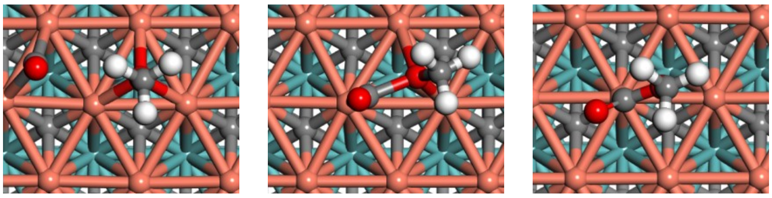
CO(T)+OCH_3(H) TSB-1(1) $COOCH_3$



CO(T)+OCH_3(F) TSB-1(2) $COOCH_3$



CO(B)+OCH_3(H) TSB-1(3) $COOCH_3$

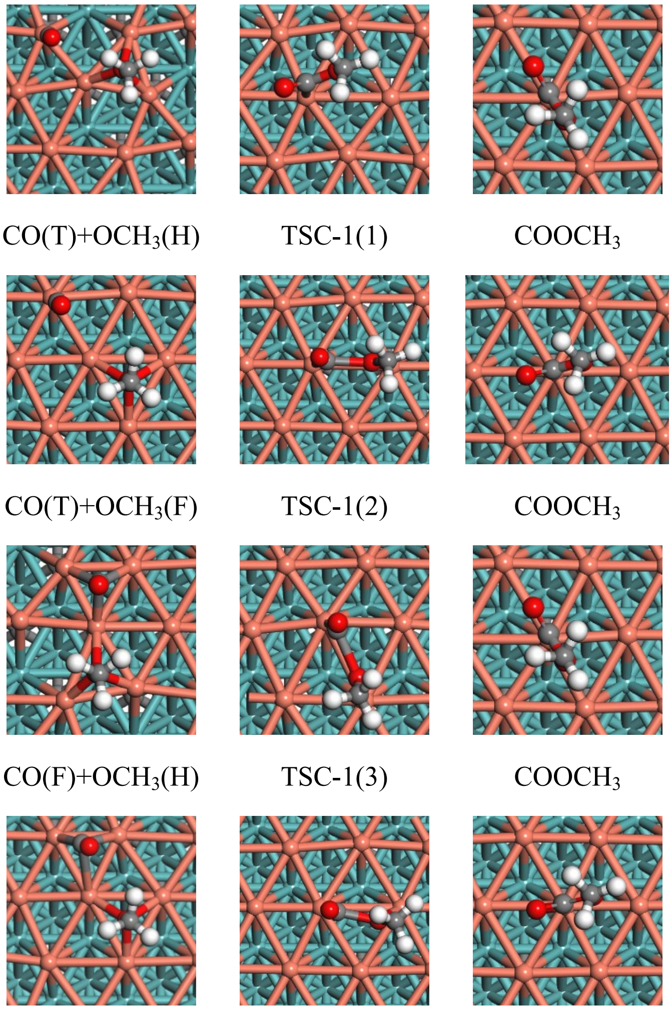


CO(B)+OCH_3(F) TSB-1(4) $COOCH_3$

Fig. S2 The structures of initial states, transition states, and final states of first elementary step for CO oxidative coupling to DMO on $Cu_{ML}/Mo_2C(001)$-C

Table S3. The activation energy (E_a) and reaction energy ($\triangle H$) of first elementary step for CO oxidative coupling to DMO on $Cu_{ML}/Mo_2C(001)$-C (kJ/mol)

	E_a	$\triangle H$
CO(T)+OCH_3(H)	91.9	30.8
CO(T)+OCH_3(F)	133.6	63.0
CO(B)+OCH_3(H)	59.3	17.2
CO(B)+OCH_3(F)	77.9	34.1



CO(T)+OCH$_3$(H) TSC-1(1) COOCH$_3$

CO(T)+OCH$_3$(F) TSC-1(2) COOCH$_3$

CO(F)+OCH$_3$(H) TSC-1(3) COOCH$_3$

CO(F) +OCH$_3$(F) TSC-1(4) COOCH$_3$

Fig. S3 The structures of initial states, transition states, and final states of first elementary step for CO oxidative coupling to DMO on Cu$_{ML}$/Mo$_2$C(001)-Mo

Table S4. The energy barrier (E_a) and reaction energy ($\triangle H$) of first elementary step for CO oxidative coupling to DMO on Cu$_{ML}$/Mo$_2$C(001)-Mo (kJ/mol)

	E_a	$\triangle H$
CO(T)+OCH$_3$(H)	156.0	82.3
CO(T)+OCH$_3$(F)	164.3	100.6
CO(F)+OCH$_3$(H)	141.7	78.2
CO(F)+OCH$_3$(F)	148.0	88.6

Microscopic kinetic details.

Microscopic kinetic is a common method to analyze the activity of catalysts, which is widely used in many catalyst researches.[1,2,3] For the CO oxidation coupling DMO reaction, the specific kinetic calculation process is as follows: first, all the elemental reactions and corresponding rate constants contained in the entire reaction process are listed in Table S5.

Table S5. The related reactions of CO oxidative coupling to DMO and the corresponding rate constants

Reaction	rate constant
$CO^* + OCH_3^* \rightarrow COOCH_3^*$	k_1
$COOCH_3^* + CO^* \rightarrow OCCOOCH_3^* + *$	k_2
$OCCOOCH_3^* + OCH_3^* \rightarrow DMO + 2*$	k_3
$COOCH_3^* + CO^* + OCH_3^* \rightarrow 2COOCH_3^* + *$	k_4
$2COOCH_3^* \rightarrow DMO + 2*$	k_5
$CO^* + CO^* \rightarrow OCCO^*$	k_6
$OCH_3^* + OCCO^* \rightarrow OCCOOCH_3^* + *$	k_7
$COOCH_3^* + OCH_3^* \rightarrow DMC + 2*$	k_8

For the surface reactions involving a gaseous species, the K_{CO} and K_{OCH3} can be obtained according to formula (3).

$$K_{eq} = \frac{pA_0}{(2\pi mkT)^{\frac{1}{2}}} = \frac{pA_0N_A}{(2\pi MRT)^{\frac{1}{2}}} \qquad (m = M / N_A, k = R / N_A) \qquad (3)$$

where p represents the pressure, A represents the effective area of the reaction site and m represents the mass. And the value of $M_{\mathrm{CO}} = 28$ g/mol and $M_{\mathrm{OCH3}} = 31$ g/mol, the Avogadro's constant N_A is 6.02×10^{-23} /mol.

According to the Eyring transition state theory and the DFT calculation results, the rate constant can be calculated by the following formula:

$$k = v_i \exp\left(\frac{-E_a}{RT}\right) \tag{4}$$

$$v_i = \frac{k_B T}{h} \frac{\prod_{i=1}^{3N} [1 - \exp(-\frac{hf_i^{IS}}{k_B T})]}{\prod_{i=1}^{3N-1} [1 - \exp(-\frac{hf_i^{TS}}{k_B T})]} \tag{5}$$

where E_a represents the activation energy of the elementary reaction, f_i^{IS} and f_i^{TS} represent the frequencies of the initial state and the transition state, respectively. And the value of the gas constant R is 8.314 J/mol·K, the value of Planck's constant h is $6.62606896 \times 10^{-34}$ J·s, and the value of the Boltzmann constant k_B is $1.3806505 \times 10^{-23}$ J/K. The equilibrium constants and reaction rate constants obtained are listed in **Table S6**.

Table S6. The reaction equilibrium constants and rate constants k (s^{-1}) in reaction pathways in the process of CO oxidative coupling reaction (375 K ≤ T≤ 415 K)

		Equilibrium constants / rate constants				
		375 K	385 K	395 K	405 K	415 K
β-$Mo_2C(001)$-Mo	K_{CO}	1.70×10^{2}	1.68×10^{2}	1.65×10^{2}	1.63×10^{2}	1.61×10^{2}
	K_{OCH3}	1.15×10^{2}	1.14×10^{2}	1.12×10^{2}	1.11×10^{2}	1.10×10^{2}
	k_1	7.07×10^{-6}	1.81×10^{-5}	4.42×10^{-5}	1.03×10^{-4}	2.31×10^{-4}
	k_2	5.72×10^{-16}	2.68×10^{-15}	1.16×10^{-14}	4.68×10^{-14}	1.76×10^{-13}
	k_3	1.14×10^{-26}	1.15×10^{-25}	1.03×10^{-24}	8.29×10^{-24}	6.03×10^{-23}
	k_4	7.88×10^{-11}	3.04×10^{-10}	1.09×10^{-9}	3.70×10^{-9}	1.18×10^{-8}
	k_5	8.42×10^{-18}	4.84×10^{-17}	2.54×10^{-16}	1.23×10^{-15}	5.53×10^{-15}
	k_6	1.44×10^{-14}	6.48×10^{-14}	2.70×10^{-13}	1.05×10^{-12}	3.80×10^{-12}
	k_7	9.44×10^{-17}	5.48×10^{-16}	2.91×10^{-15}	1.42×10^{-14}	6.46×10^{-14}
	k_8	3.94×10^{-13}	1.77×10^{-12}	7.35×10^{-12}	2.85×10^{-11}	1.04×10^{-10}
$Cu_{ML}/Mo_2C(001)$-C	K_{CO}	1.70×10^{2}	1.68×10^{2}	1.65×10^{2}	1.63×10^{2}	1.61×10^{2}
	K_{OCH3}	1.15×10^{2}	1.14×10^{2}	1.12×10^{2}	1.11×10^{2}	1.10×10^{2}
	k_1	2.30×10^{4}	3.75×10^{4}	5.98×10^{4}	9.29×10^{4}	1.41×10^{5}
	k_2	2.86×10^{-8}	9.51×10^{-8}	2.97×10^{-7}	8.79×10^{-7}	2.47×10^{-6}
	k_3	8.82×10^{-5}	2.23×10^{-4}	5.39×10^{-4}	1.24×10^{-3}	2.76×10^{-3}
	k_4	4.46×10^{-5}	1.38×10^{-4}	4.05×10^{-4}	1.13×10^{-3}	2.99×10^{-3}
	k_5	7.56×10^{-14}	3.33×10^{-13}	1.36×10^{-12}	5.18×10^{-12}	1.85×10^{-11}
	k_8	8.03×10^{-14}	4.33×10^{-13}	2.15×10^{-12}	9.85×10^{-12}	4.20×10^{-11}

When the CO oxidation coupling to the DMO reaction reaches chemical equilibrium, the reaction species and the free site θ* satisfy the following relationship:

$$\theta_{CO}+\theta_{OCH_3}+\theta_{COOCH_3}+\theta_{OCCOOCH_3}+\theta_{OCCO}+\theta^{*}=1 \tag{6}$$

Among them, θ_{CO}, θ_{OCH3}, θ_{COOCH3}, $\theta_{OCCOOCH3}$ and θ_{OCCO} represent the surface coverage of CO, OCH_3, $COOCH_3$, $OCCOOCH_3$ and OCCO, respectively, which is obtained by the chemical equation and steady-state equilibrium principle of the reaction. The corresponding calculation formula and results are as follows:

$$\theta_{CO} = P_{CO} K_{CO} \theta^* \tag{7}$$

$$\theta_{OCH_3} = P_{OCH_3} K_{OCH_3} \theta^* \tag{8}$$

$$\theta_{COOCH_3} : \frac{d\theta_{COOCH_3}}{dt} = k_1 \theta_{OCH_3} \theta_{CO} + k_4 \theta_{OCH_3} \theta_{CO} - k_2 \theta_{COOCH_3} \theta_{CO} - k_5 \theta_{COOCH_3}^2 - k_8 \theta_{OCH_3} \theta_{COOCH_3} = 0 \tag{9}$$

$$\theta_{OCCOOCH_3} : \frac{d\theta_{OCCOOCH_3}}{dt} = k_2 \theta_{COOCH_3} \theta_{CO} + k_7 \theta_{OCH_3} \theta_{OCCO} - k_3 \theta_{OCCOOCH_3} \theta_{OCH_3} = 0 \tag{10}$$

$$\theta_{OCCO} : \frac{d\theta_{OCCO}}{dt} = k_6 \theta_{CO}^2 - k_7 \theta_{OCH_3} \theta_{OCCO} = 0 \tag{11}$$

Table S7. The surface coverage of different species (375 K ≤ T ≤ 415 K)

		375 K	385 K	395 K	405 K	415 K
	θ^*	3.22×10^{-20}	1.05×10^{-19}	3.24×10^{-19}	9.45×10^{-19}	2.62×10^{-18}
	θ_{CO}	1.51×10^{-17}	4.88×10^{-17}	1.48×10^{-16}	4.27×10^{-16}	1.17×10^{-15}
	θ_{OCH_3}	7.32×10^{-18}	2.36×10^{-17}	7.19×10^{-17}	2.07×10^{-16}	5.66×10^{-16}
β-$Mo_2C(001)$-Mo	θ_{COOCH_3}	9.63×10^{-12}	2.08×10^{-11}	4.30×10^{-11}	8.59×10^{-11}	1.66×10^{-10}
	$\theta_{OCCOOCH_3}$	1.00×10^{0}	1.00×10^{0}	1.00×10^{0}	1.00×10^{0}	1.00×10^{0}
	θ_{OCCO}	4.76×10^{-15}	1.19×10^{-14}	2.83×10^{-14}	6.47×10^{-14}	1.42×10^{-13}
	θ^*	5.55×10^{-12}	9.23×10^{-12}	1.50×10^{-11}	2.37×10^{-11}	3.68×10^{-11}
	θ_{CO}	2.60×10^{-9}	4.27×10^{-9}	6.85×10^{-9}	1.07×10^{-8}	1.64×10^{-8}
$Cu_{ML}/Mo_2C(001)$-C	θ_{OCH_3}	1.26×10^{-9}	2.07×10^{-9}	3.32×10^{-9}	5.20×10^{-9}	7.96×10^{-9}
	θ_{COOCH_3}	9.99×10^{-1}	9.99×10^{-1}	9.99×10^{-1}	9.99×10^{-1}	9.99×10^{-1}
	$\theta_{OCCOOCH_3}$	6.69×10^{-4}	8.78×10^{-4}	1.14×10^{-3}	1.46×10^{-3}	1.84×10^{-3}

The rate of formation of the final product can be obtained according to formulas (14) and (15), and the results are listed in Table 4. After obtaining the formation rate of the target product DMO and the by-product DMC, the selectivity $S_{\mathrm{DMO/DMC}}$ for the formation of DMO on the catalyst can be calculated by the following formula (14).

$$r_{DMO} = k_3\theta^2_{COOCH_3} + k_5\theta_{OCCOOCH_3}\theta_{OCH_3} \tag{12}$$

$$r_{DMC} = k_6\theta_{COOCH_3}\theta_{OCH_3} \tag{13}$$

$$s_{DMO/DMC} = \frac{r_{DMO/DMC}}{r_{DMC} + r_{DMC}} \tag{14}$$

Where r_{DMO} and r_{DMC} represent the generation rates of DMO and DMC, respectively.

References

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