## **Supporting Information Text**

Theoretical computation of C-C coupling reactions by different C1

intermediates at Cu<sub>n</sub> and Cu<sub>n-1</sub>Ag clusters supporting on TiO<sub>2</sub>

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Figure S1 The electronic structures of the Cu-Ag clusters.

Figure S2 The two \*CO and \*CO coupling forming C-C bond energy diagram and the corresponding structures on the  $Cu_8@TiO_2$ .

- Figure S3 The two \*CO and \*COH coupling forming C-C bond energy diagram and the corresponding structures on the Cu<sub>8</sub>@TiO<sub>2</sub>.
- Figure S4 The two \*CO and \*CHO coupling forming C-C bond energy diagram and the corresponding structures on the Cu<sub>8</sub>@TiO<sub>2</sub>.

- Figure S5 The two \*CO and \*CH<sub>2</sub> coupling forming C-C bond energy diagram and the corresponding structures on the  $Cu_8@TiO_2$ .
- Figure S6 The two \*CO and \*CH<sub>3</sub> coupling forming C-C bond energy diagram and the corresponding structures on the Cu<sub>8</sub>@TiO<sub>2</sub>.
- Figure S7 The two \*COH and \*COH coupling forming C-C bond energy diagram and the corresponding structures on the Cu<sub>8</sub>@TiO<sub>2</sub>.
- Figure S8 The two \*COOH and \*CH<sub>3</sub> coupling forming C-C bond energy diagram and the corresponding structures on the  $Cu_8@TiO_2$ .
- Figure S9 The two \*CHO and \*CHO coupling forming C-C bond energy diagram and the corresponding structures on the Cu<sub>8</sub>@TiO<sub>2</sub>.

Figure S10 The two \*CHO and \*CH<sub>3</sub> coupling forming C-C bond energy diagram and the corresponding structures on the  $Cu_8@TiO_2$ .

- Figure S11 The two  $*CH_2$  and  $*CH_2$  coupling forming C-C bond energy diagram and the corresponding structures on the Cu<sub>8</sub>@TiO<sub>2</sub>.
  - Figure S12 The two  $*CH_2O$  and  $*CH_2O$  coupling forming C-C bond energy diagram and the corresponding structures on the Cu<sub>8</sub>@TiO<sub>2</sub>.

Table S1 The adsorption energies (Eads, in eV) of \*CO and \*CO  $\times$  \*CO and \*COH  $\times$  \*CO and \*CHO on the Cu<sub>7</sub>Ag@TiO<sub>2</sub>  $\sim$  Cu<sub>12</sub>Ag@TiO<sub>2</sub> and Cu<sub>19</sub>Ag@TiO<sub>2</sub> respectively.

		elementary reactions	$\Delta E_{ads}(eV)$
Cu7Ag@TiO2	R1	*CO+*CO→*OCCO	-0.3853665
	R2	*СО+*СОН→*ОССОН	-3.76918676
	R3	*СО+*СНО→*ОССНО	-2.93684903
Cu <sub>12</sub> Ag@TiO <sub>2</sub>	R1	*CO+*CO→*OCCO	-1.39562239
	R2	*СО+*СОН→*ОССОН	-2.28730576
	R3	*СО+*СНО→*ОССНО	-1.81641165
Cu <sub>19</sub> Ag@TiO <sub>2</sub>	R1	*CO+*CO→*OCCO	-0.89603505
	R2	*СО+*СОН→*ОССОН	-2.7606876
	R3	*СО+*СНО→*ОССНО	-2.52910628