Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Catalytic performance of Pd_n(n=1, 2, 3, 4 and 6) clusters supported on $TiO_{2\text{-}V}$ for the formation of dimethyl oxalate via CO catalytic coupling reaction: A theoretical study

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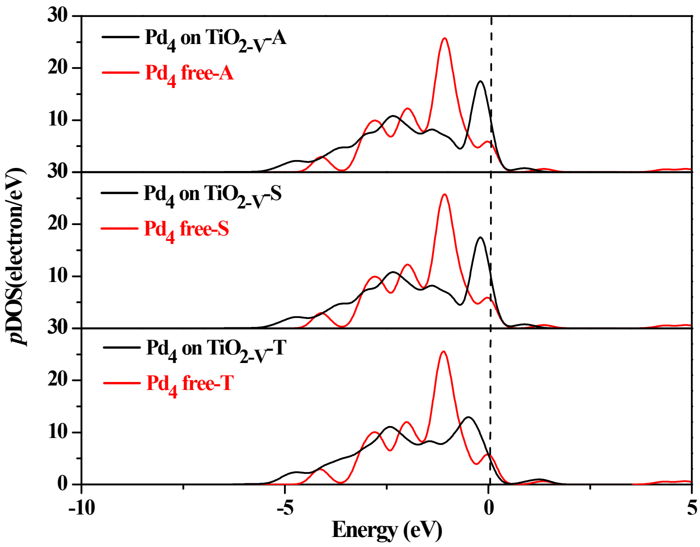

Fig. S1 Partial density of states (*p*DOS) for Pd_4 cluster on $TiO_{2\text{-}V}$ with different multiplicities. Black line represents Pd_4 cluster supported on $TiO_{2\text{-}V}$, and red line represents free Pd_4 cluster. The suffix A, S and T represents different spin states, A shows that spin state is not fixed, S shows that spin state is singlet, and T shows that spin state is triplet.

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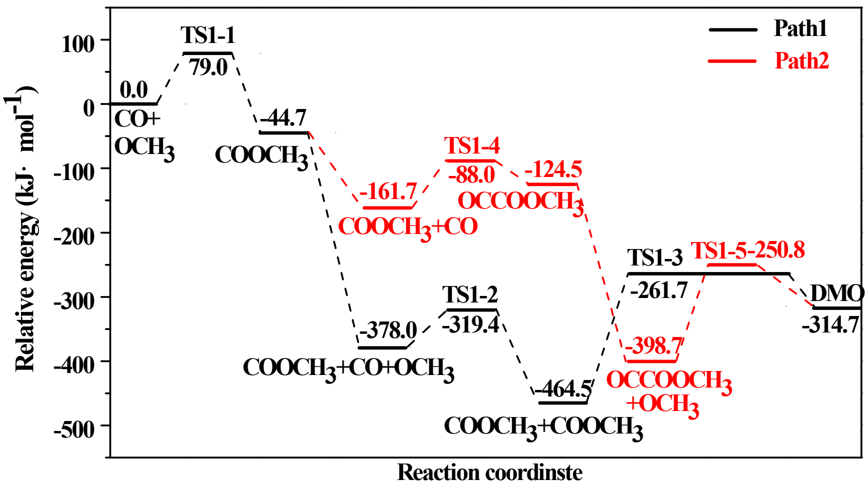

Fig. S2 The potential energy profile for the CO catalytic coupling reaction to DMO on Pd_2/TiO_{2-V}.

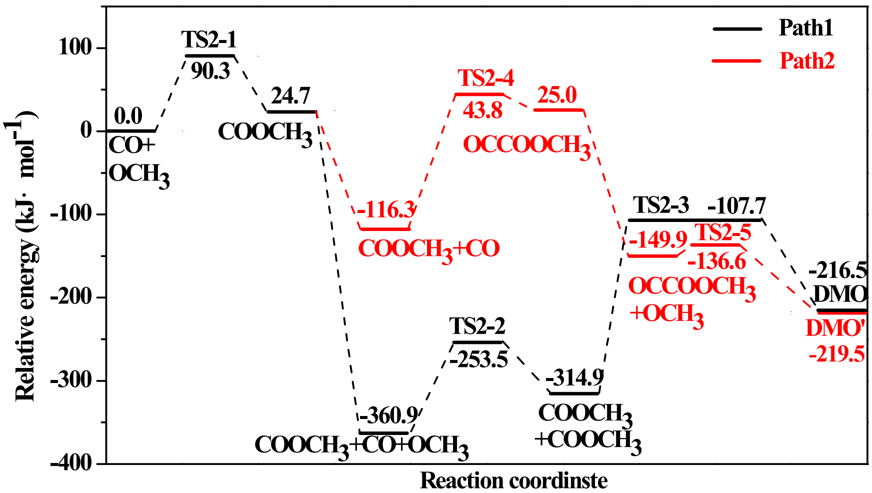

Fig. S3 The potential energy profile for the formation of DMO on Pd_3/TiO_{2-V}.

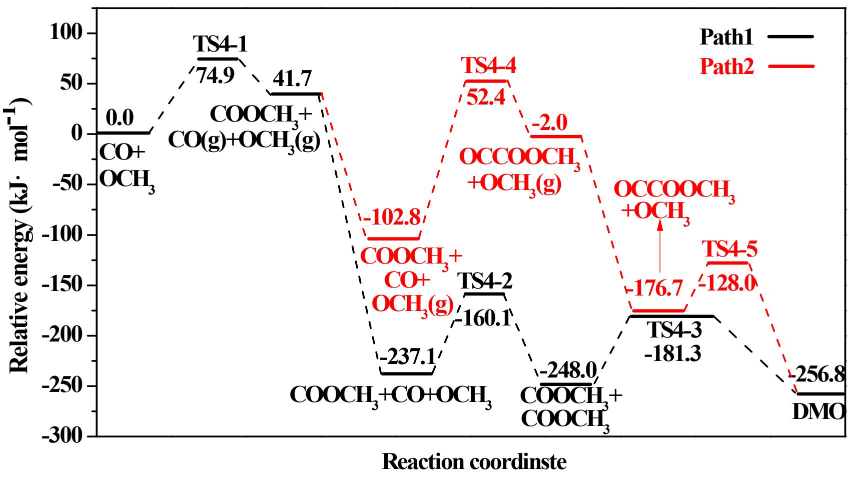

Fig. S4 The potential energy profile for the CO catalytic coupling reaction on Pd_4/TiO_{2-V}.[1]

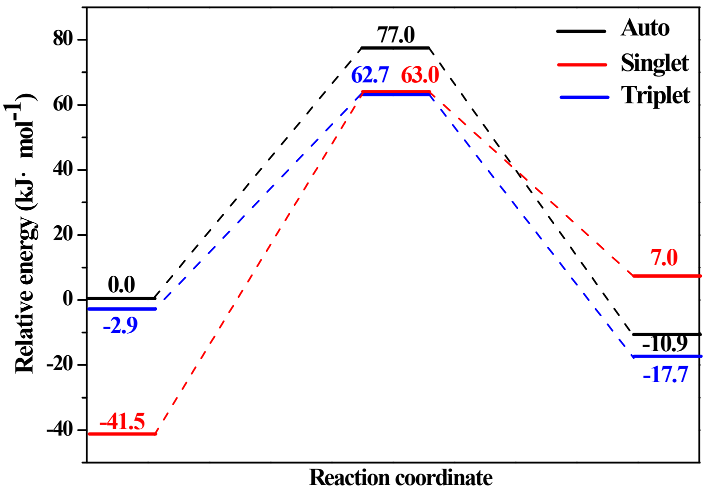

Fig. S5 The potential energy profile for the rate-determining step ($COOCH_3$+CO+OCH_3 → $COOCH_3$+$COOCH_3$) on Pd_4/TiO_{2-V} with multiplicity of singlet, triplet and auto.

Table S1 Adsorption energies ($kJ\cdot mol^{-1}$) of stable species on the Pd_2/TiO_{2}-$_v$, Pd_3/TiO_{2}-$_v$, Pd_4/TiO_{2}-$_v$ and Pd_6/TiO_{2}-$_v$.

	E_{ads} (Pd_2/TiO_2-$_v$)	E_{ads} (Pd_3/TiO_2-$_v$)	E_{ads} (Pd_4/TiO_2-$_v$)	E_{ads} (Pd_6/TiO_2-$_v$)
CO-OCH_3	-345.2	-418.0	-441.2	-368.9
$COOCH_3$	-250.3	-253.2	-259.9	-218.2
$COOCH_3$-CO	-367.3	-394.8	-404.4	-358.5
$OCCOOCH_3$	-284.3	-207.6	-257.7	-259.0
$OCCOOCH_3$-OCH_3	-558.4	-382.4	-432.4	-472.9
$COOCH_3$-CO-OCH_3	-583.6	-639.3	-538.7	-602.9
$COOCH_3$-$COOCH_3$	-530.5	-453.8	-410.1	-453.2
DMO	-34.0	-8.6	-72.2	-79.1

References:

[1] Y. T. Cao, L. X. Ling, H. Lin, M. H. Fan, P. Liu, R. G. Zhang and B. J. Wang, *Comput. Mater. Sci.,* 2019, **159**, 1-11.