*Supporting information*

# A systematic theoretical study of water gas shift reaction on $Pt/ZrO_2$ interface and Pt(111) face: key role of potassium additive

Yan-Xin Wang , Gui-Chang Wang*

( Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education) and the Tianjin key Lab and Molecule-based Material Chemistry, College of Chemistry, Nankai University, Tianjin 300071, P. R. China)

*Corresponding author. Gui-Chang Wang: E-mail: wangguichang@nankai.edu.cn

Telephone: +86-22-23503824 (O) Fax: +86-22-23502458

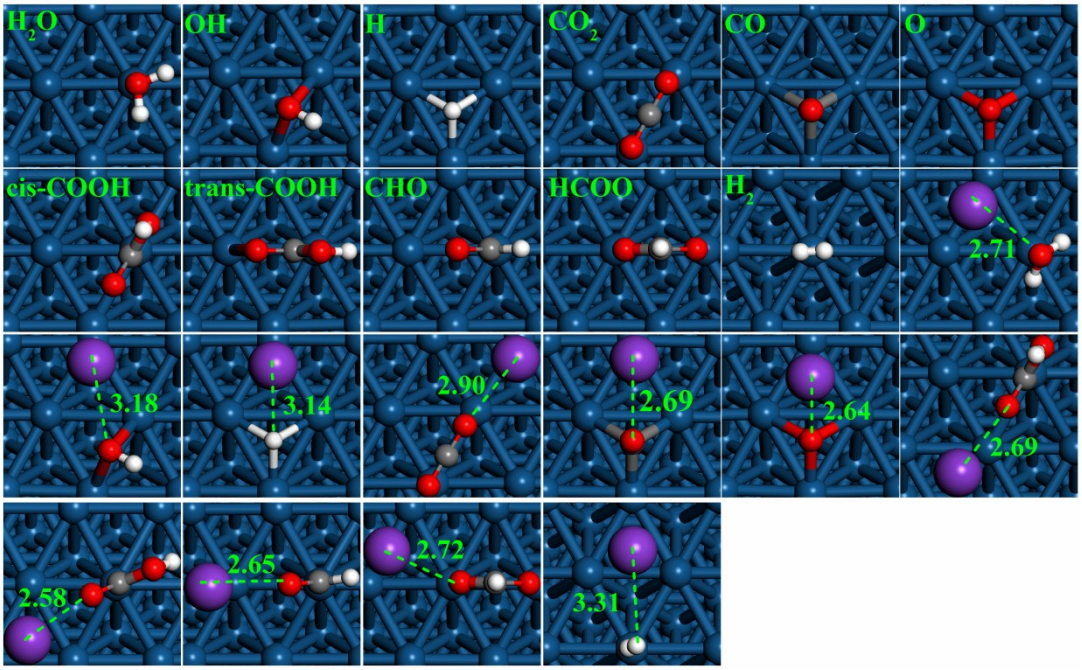


**Fig. S1** Optimized structures of reaction intermediates on the clean and K-modified Pt(111) surfaces. The red, blue, white and purple balls represent O, Pt, H and K atoms, respectively.

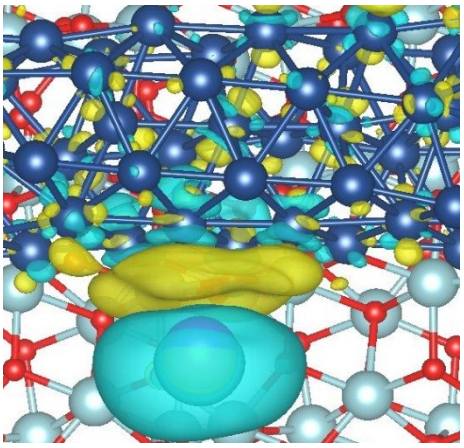

**Fig. S2** Charge distribution between K and $Pt_{40}/ZrO_2$ substrate. The yellow and cyan isosurfaces stand for the accumulation and the depletion of electron density, respectively.

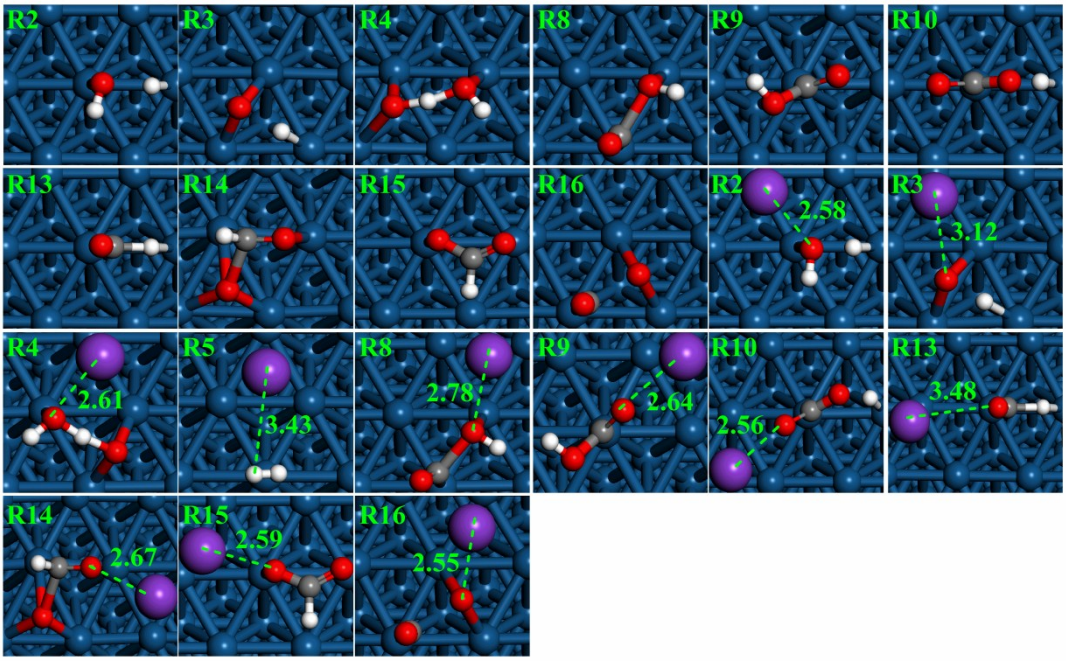


**Fig. S3** Transition state (TS) structures of elementary steps (labeled the same way as in Table S1) on the clean and K-modified Pt(111) surfaces. The red, white, dark-blue and purple balls represent O, H, Pt and K atoms, respectively.

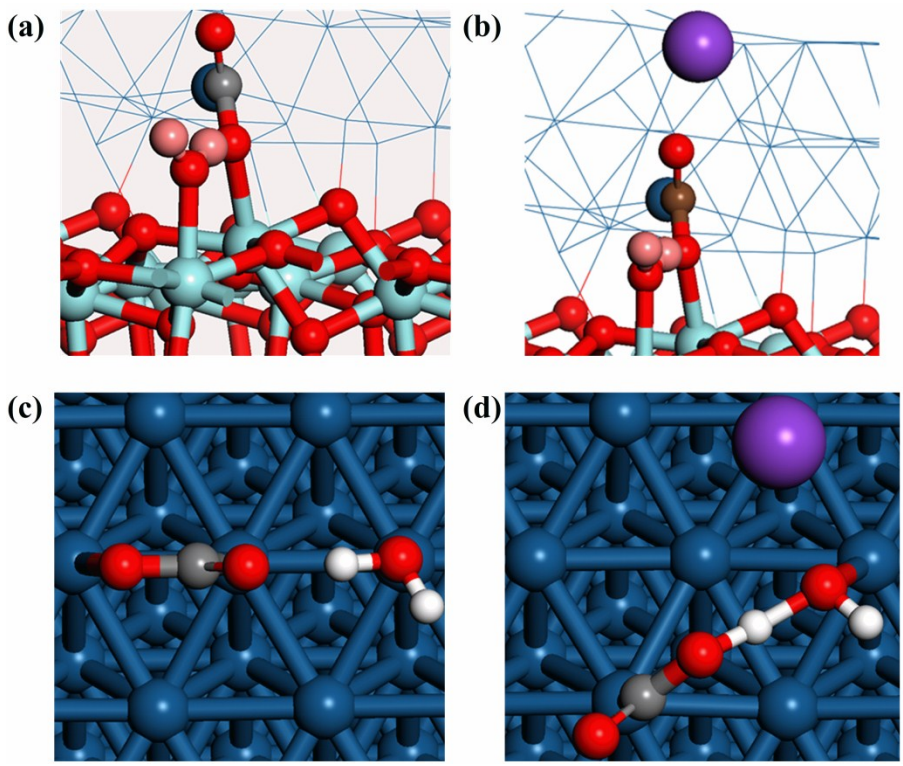


**Fig. S4** Final state (FS) structures of COOH+OH=$CO_2$+$H_2O$ reaction on the (a) clean $Pt_{40}/ZrO_2$ interface; (b) K-modified $Pt_{40}/ZrO_2$ surface and (c) clean Pt(111) surface as well as Transition state (TS) structure on the (d) K-modified Pt(111) surface. The red, white, dark-blue, light-blue and purple balls represent O, H, Pt, Zr and K atoms, respectively.

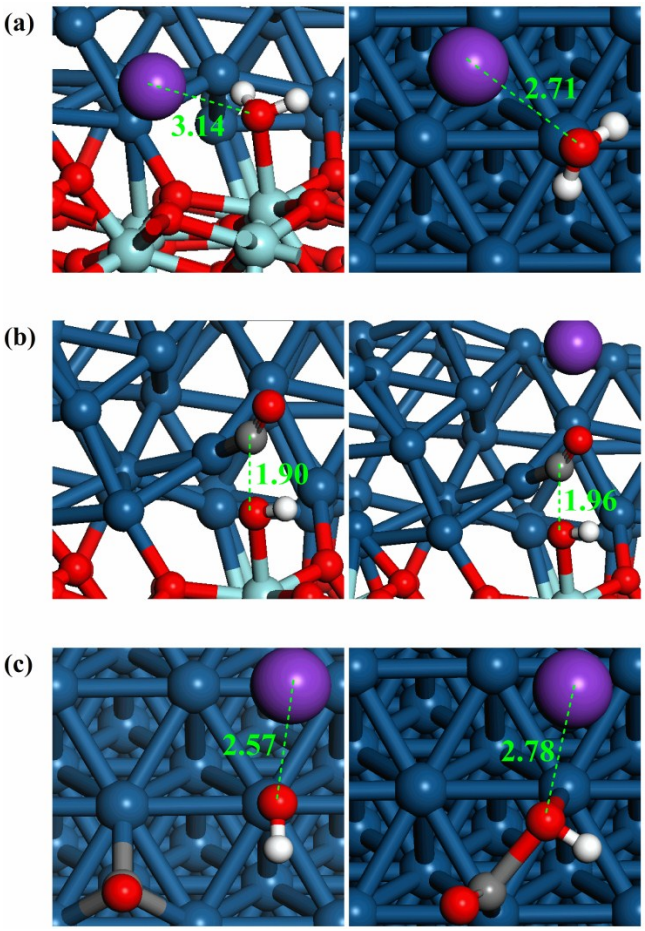


**Fig. S5** (a) Optimized structures of $H_2O$ on K-modified $Pt_{40}/ZrO_2$ and Pt(111) models. (b) Optimized structures of TS for CO+OH→COOH on clean and K-modified $Pt_{40}/ZrO_2$. (c) Optimized structures of IS and TS for CO+OH→COOH on K-modified Pt(111).

**Table S1** Calculated energy barriers ($E_a$), reaction energies ($\Delta E$), and the breaking or forming bond lengths of TSs ($d$) of the elementary steps on clean and K-modified Pt(111) surfaces[a]

| | | Pt(111) | | | K/Pt(111) | | |
|---|---|---|---|---|---|---|---|
| | Elementary steps | $E_a$/eV | $\Delta E$/eV | $d$/Å | $E_a$/eV | $\Delta E$/eV | $d$/Å |
| R1 | $H_2O(g)+*\rightarrow H_2O*$ | -- | –0.52 | -- | -- | –0.87 | -- |
| R2 | $H_2O*\rightarrow OH*+H*$ | 0.98 | 0.84 | 1.73 | 0.95 | 0.66 | 1.57 |
| R3 | $OH*+*\rightarrow O*+H*$ | 1.03 | 0.14 | 1.58 | 0.96 | 0.10 | 1.46 |
| R4 | $OH*+OH*\rightarrow O*+H_2O*$ | 0.40 | –0.16 | -- | 0.12 | –0.36 | -- |
| R5 | $H*+H*\rightarrow H_2*+*$ | -- | 0.90 | -- | 1.00 | 0.84 | 0.78 |
| R6 | $H_2*\rightarrow H_2(g)+*$ | -- | 0.09 | -- | -- | 0.11 | -- |
| R7 | $CO(g)+*\rightarrow CO*$ | -- | –1.87 | -- | -- | –2.27 | -- |
| R8 | $CO*+OH*\rightarrow$cis-$COOH*+*$ | 0.31 | –0.33 | 1.93 | 0.76 | 0.04 | 1.84 |
| R9 | cis-$COOH*\rightarrow$trans-$COOH*$ | 0.39 | –0.08 | -- | 0.34 | –0.31 | -- |
| R10 | $COOH*+*\rightarrow CO_2*+H*$ | 0.73 | –0.10 | 1.54 | 0.68 | 0.31 | 1.74 |
| R11 | $COOH*+*OH\rightarrow CO_2*+H_2O*$ | -- | -- | -- | 0.20 | –0.38 | -- |
| R12 | $CO_2*\rightarrow CO_2(g)+*$ | -- | 0.49 | -- | -- | 1.91 | -- |
| R13 | $CO*+H*\rightarrow CHO*+*$ | 1.06 | 0.76 | 1.29 | 0.96 | 0.49 | 1.40 |
| R14 | $CHO*+O*\rightarrow HCOO*+*$ | 0.75 | –1.11 | 1.89 | 0.82 | –1.17 | 1.93 |
| R15 | $HCOO*+*\rightarrow CO_2*+H*$ | 1.03 | 0.10 | 1.13 | 0.58 | –0.27 | 1.12 |
| R16 | $CO*+O*\rightarrow CO_2*+*$ | 0.91 | –0.61 | 1.95 | 0.89 | –0.72 | 2.01 |

**Table S2** The entropic energies of species ($H_2O$, CO, $CO_2$ and $H_2$) in gas phase (TS), in adsorbed states on clean $Pt_{40}/ZrO_2$ (TS1), K-modified $Pt_{40}/ZrO_2$ (TS2), clean Pt(111) (TS3) and K-modified Pt(111) (TS4) as well as the change of entropy energies from gas phase to the adsorption state on clean $Pt_{40}/ZrO_2$ (TΔS1), K-modified $Pt_{40}/ZrO_2$ (TΔS2), clean Pt(111) (TΔS3) and K-modified Pt(111) (TΔS4) (T = 500 K)

| | $H_2O$ | CO | $CO_2$ | $H_2$ |
|---|---|---|---|---|
| TS (eV) | 1.07 | 1.10 | 1.22 | 0.76 |
| TS1 (eV) (((e((( | 0.28 | 0.32 | 0.44 | 0.39 |
| TS2 (eV) | 0.25 | 0.31 | 0.37 | 0.39 |
| TS3 (eV) | 0.61 | 0.26 | 0.71 | 0.39 |
| TS4 (eV) | 0.61 | 0.23 | 0.71 | 0.39 |
| TΔS1 (eV) | 0.79 | 0.78 | 0.78 | 0.37 |
| TΔS2 (eV) | 0.82 | 0.79 | 0.85 | 0.37 |
| TΔS3 (eV) | 0.46 | 0.84 | 0.51 | 0.37 |
| TΔS4 (eV) | 0.46 | 0.87 | 0.51 | 0.37 |

**Table S3** Bader charges of K and O at the TSs in $H_2O$ and COOH dissociation on $Pt_{40}/ZrO_2$ and Pt(111) models (Unit in e)

| model | TS in $H_2O$ dissociation | | TS in COOH dissociation | |
|---|---|---|---|---|
| | K | O/OH | K | $O/CO_2$ |
| $Pt_{40}/ZrO_2$ | +0.88 | –1.66 | +0.88 | –1.93 |
| Pt(111) | +0.86 | –1.52 | -- | -- |