## Theoretical insight into the relevance between the oxidation states of $CeO_2$ supported $Pt^{4+/2+/1+/0/2-}$ and their

## HER performance

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Fig. S1 The three possible  $Pt_2/CeO_2$  structures, (a)  $Pt_{2c}+Pt_{4c}$ , (b)  $Pt_{3c}+Pt_{3c}$  and (c)  $Pt_{3c}+Pt_{4c}$ . The Ce, O and Pt atoms are denoted by yellow, red and light blue balls, respectively. The silver atoms are the neatest O atoms of Pt atoms.



Fig. S2 The five structures of local spin minima for  $Pt^{1+}/CeO_2$ .



Fig. S3 The optimized structures of (a)  $Pt^{4+}/CeO_2$  and (b)  $Pt^{2+}/CeO_2$ . The Ce, O, Pt and H atoms are denoted by yellow, red, light blue and dark blue balls, respectively. The silver atoms are the neatest O atoms of Pt atoms.



Fig. S4 The PDOS of  $Pt^{4+}$ ,  $Pt_{3c}^{2+}$  and  $Pt_{4c}^{2+}$ .

Table. S1 The number of Ce <sup>3+</sup> ions with their magnetic mor	ment.
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Pt <sup>1+</sup> /CeO <sub>2</sub>		(Pt-H) <sup>1+</sup> /CeO <sub>2</sub>		(H-Pt-H) <sup>0</sup> /CeO <sub>2</sub>	
Ce <sup>3+</sup>	Magnetic moment	Ce <sup>3+</sup>	Magnetic moment	Ce <sup>3+</sup>	Magnetic moment
Ce <sub>18</sub>	0.959 μΒ	Ce <sub>18</sub>	0.971 μB	Ce <sub>18</sub>	0.968 µB
Ce <sub>33</sub>	0.946 µB	Ce <sub>33</sub>	0.941 μB	Ce <sub>36</sub>	0.966 µB
Ce <sub>36</sub>	0.927 µB	Ce <sub>36</sub>	0.954 μB		
Pt <sup>0</sup> /CeO <sub>2</sub>		(Pt-H) <sup>1+</sup> /CeO <sub>2</sub>		(H-Pt-H) <sup>0</sup> /CeO <sub>2</sub>	
Ce <sup>3+</sup>	Magnetic moment	Ce <sup>3+</sup>	Magnetic moment	Ce <sup>3+</sup>	Magnetic moment
-	-	Ce <sub>33</sub>	0.946 µB	-	-
Pt <sup>2-</sup> /CeO <sub>2</sub>		(Pt-H)/CeO <sub>2</sub>		(H-Pt-H)/CeO <sub>2</sub>	
Ce <sup>3+</sup>	Magnetic moment	Ce <sup>3+</sup>	Magnetic moment	Ce <sup>3+</sup>	Magnetic moment
-	-	Ce <sub>30</sub>	0.968 µB	-	-