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Single atom detachment from Cu clusters, and diffusion and trapping on CeO_2(111): implications in Ostwald ripening and atomic redispersion†

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Ostwald ripening is a key mechanism for sintering of highly dispersed metal nanoparticles in supported catalysts. However, our microscopic understanding of such processes is still primitive. In this work, the atomistic mechanism of the Ostwald ripening of Cu on CeO_2(111) is examined *via* density functional theory calculations. In particular, the detachment of a single Cu atom from ceria supported Cu_n (n = 2–10, 12, 14, 16, 18, and 20) clusters and trapping on the CeO_2(111) surface is investigated in the absence and presence of CO adsorption. It is shown that the adsorption of CO on Cu reduces its detachment energy, which helps in the formation of single atom species on CeO_2(111). In addition, the Cu_1–CO species is found to diffuse on the CeO_2(111) surface with a much lower barrier than a Cu atom. These observations suggest an efficient mechanism for the Ostwald ripening of Cu clusters supported on ceria in the presence of CO. It is further predicted that the Cu_1–CO species can eventually migrate to a step site on ceria, generating a stable single-atom motif with a relatively larger binding energy. Finally, the single Cu atom catalyst is shown to possess high activity for the oxygen reduction reaction.

1. Introduction

2. Computational methods

F C $_n$ C $_2$(111), E :

$$E = [nE(\mathrm{C}) + E(\mathrm{C}\ _2) - E(\mathrm{C}\ _n/\mathrm{C}\ _2)]/n \quad (2)$$

E(C $_2$) E(C $_n$/C $_2$) C $_2$(111) C $_2$(111) C $_n$, C (E)

$$E = E(\mathrm{C}\ _{n-1}/\mathrm{C}\ _2) + E(\mathrm{C}\ /\mathrm{C}\ _2) - E(\mathrm{C}\ _n/\mathrm{C}\ _2) - E(\mathrm{C}\ _2) \quad (3)$$

E(C $_{n-1}$/C $_2$) E(C /C $_2$) C $_2$(111) C $_{n-1}$ C $_1$ C $_1$–C C C (E (C)) :

$$E(\mathrm{C}) = E(\mathrm{C}\ _{n-1}/\mathrm{C}\ _2) + E(\mathrm{C}\ _1\text{–}\mathrm{C}\ /\mathrm{C}\ _2) - E(\mathrm{C}\ _n\text{–}\mathrm{C}\ /\mathrm{C}\ _2) - E(\mathrm{C}\ _2) \quad (4)$$

E(C $_1$–C /C $_2$) E(C $_n$–C /C $_2$) C $_2$(111) C $_1$–C C $_n$ C C C $_n$ C $_2$(111) :

$$E = E(\mathrm{C}\ _n/\mathrm{C}\ _2) - E(\mathrm{C}\ _n) - E(\mathrm{C}\ _2) \quad (5)$$

E(C $_n$/C $_2$), E(C $_n$) E(C $_2$) C $_n$ C $_2$, C $_n$, C $_2$, (CI- EB)[55,56] C C $_1$–C C $_2$(111). ff ff ff 10^{-4} 0.05 $^{-1}$

3. Results and discussion

3.1 Stabilit and disintegration of C cl sters on CeO$_2$(111)

C ff C –C C $_n$ (n = 2–10, 12, 14, 16, 18, 20) (F . 1( )), (2D) (3D)[57–63] C C $_2$(111).

C ff Fig. 2. I C n 2 (1.12) 8 (2.14). F 9 20 E n C $_n$ n = 35, 55, 100 230) E 3.69 3.48 (. 64) (F . 1 2†). C –C C C C C $_2$(111) F . 1( ). I C C . F C $_{10}$ C –C C $_2$(111) 2.45 2.67 C C $_2$(111) −2.02 – −6.72 (1†), C C $_2$(111). F , C $_8$ C $_2$(111) C $_8$ −3.71 (−4.44) . I C $_8$ C $_2$. A C −2.55 C C F . 2. I C – I C $_2$(111). C $_2$ [34] ff 1.44 C $_3$. H ff 0.33 14–20 C C C $_2$(111). F . 3 C C $_n$ C $_2$(111) C $_2$(111). I C C $_2$(111). ff

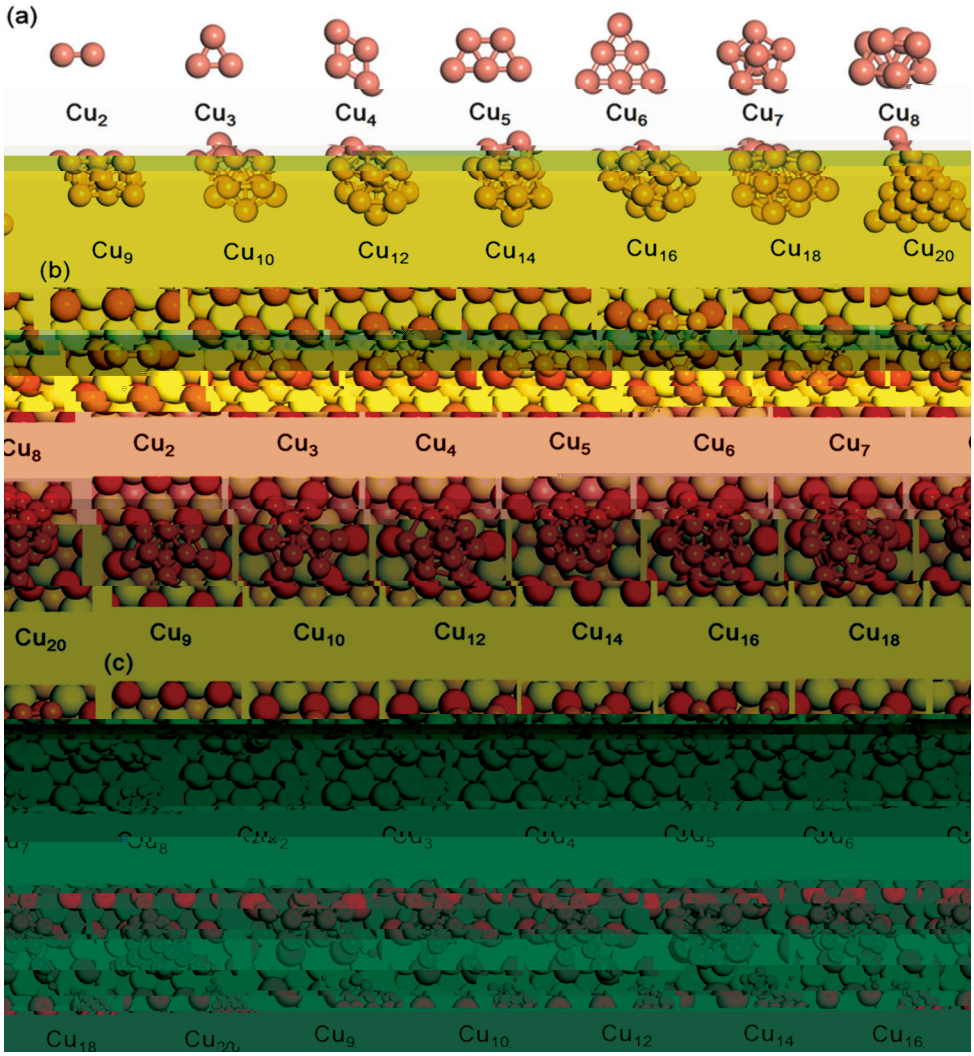

Fig. 1 (a) Stable structures of the isolated Cu_n clusters (n = 2–10, 12, 14, 16, 18, and 20). (b) Optimized structures of the Cu clusters on CeO_2(111) and (c) optimized structures of CO adsorption on the corner Cu atom of Cu clusters on CeO_2(111). Color scheme: Ce, yellow; surface O, red; subsurface O, coral; Cu, bronze; C, grey.

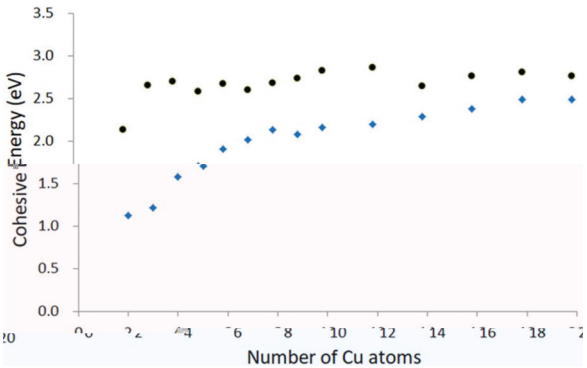

Fig. 2 Calculated cohesive energies of CeO_2(111) supported Cu clusters (black) and the corresponding gas-phase Cu clusters (blue).

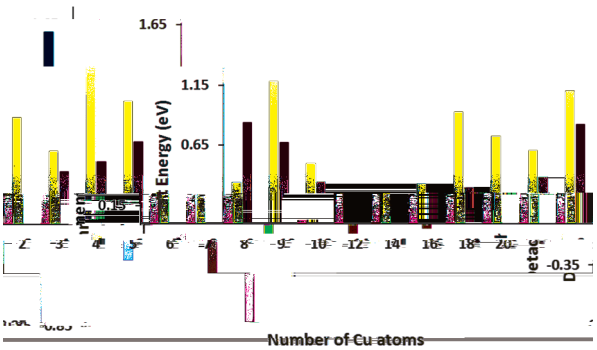

Fig. 3 Calculated detachment energies of a Cu atom from CeO_2(111) supported Cu_n clusters (n = 2–10, 12, 14, 16, 18, and 20) with (green column) and without (red column) CO adsorption. Since the CO adsorption on Cu_5 and Cu_6 results in a spontaneous dissociation of clusters to form a Cu_1–CO complex nearby on CeO_2(111), the detachment energies in the presence of CO are not included.

. F C 2, 0.34 . B C C 3, 1.18 . C 5 −0.3 , C F *n* 6–10, *n* 10, C C C 2(111) C *n* C *n*−1 + C 1, C C *n*−1 3.† B C C 2(111) ffi . H - C . I ,

3.2 Infl ence of CO adsorption on C detachment from CeO_2(111)

I ff C C C - C C 2(111). F . 1(•) C *n* (*n* = 2–10, 12, 14, 16, 18, 20) C 2(111) C C . F , C– 1.16 0.02 C–C 1.81 . H , C C . H , C D C C 2(111) C C C . A F . 3 ( ), C - C 2, ff . F C 7 C 9, 0.33 0.72 −0.82 −0.04 C , C - C 2D C 5 C 6 C 1–C C 2(111). (A) AIMD, [65,66] C *n*–C C *n*−1 + C 1–C C 1–C C *n*−1 C . I , C 5 C 6 . A 3.† A 30,34 F C *n* (*n* = 5–20) (−2.40) C 34 F A , AIMD A A C 32 A 1–C C C 2(111), C −2.26 . A 1,† C C −1.50 – −0.50 . C . F , (−0.50) C C 7 −0.82 ff C C C 7 C −0.93 . I , C C –C . F C 14, C C C 2.39 2.53 2.64 2.65 C I , C *n* C 2 C C *n* . H , ff C C 8 . I , 4,† ff ff . F C 8, C (F . 3†), - 4† C 8 H , Δ*E*, ff *E* (C), *E* (C), −0.50 −1.17 , C C C 2(111). ff C C C 2(111) C F . 4 0.30 0.11 C 1 (,) . 7 (, -). F C 8 C 2(111) C C C 2.52, 2.43, 2.60 . F

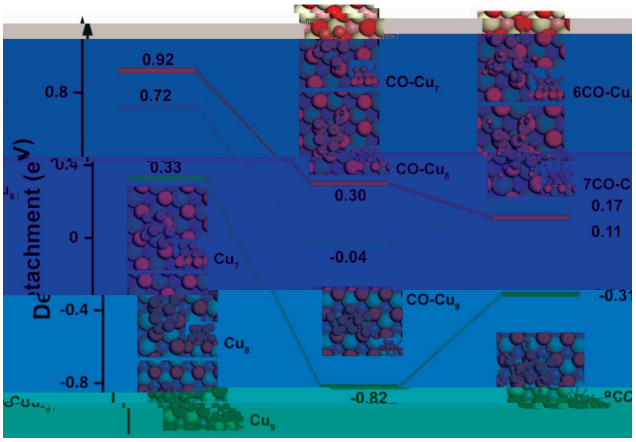

Fig. 4 Calculated detachment energies of a Cu atom from $CeO_2(111)$ supported Cu_n (n = 7–9) with $(CO)_m$ (m = 0, 1, and 7) adsorption. Color scheme: Ce, yellow; surface O, red; subsurface O, coral; Cu, bronze; C, grey.

(AIMD) C

3.3 Migration of the C atom and C 1–CO comple on ceria

. H ff C C 1–C C 2(111). A 1, C C 2(111) (F . 5 C −2.55 ∼−2.32 .[67] C – 2.03, 2.03 2.07 . F EB (F . 6), ff C (F . 4†) 0.95 (F . 6). A 1.06 . C C 2(111) ffi ff - (0.14)[34] A (0.26)[30] C 2(111). (1.28) C

C C 8, 2.66, 2.50, 2.81 C C 8, 2.64, 2.55 2.84 C C C C C C C C C –C C −1.00 C ff C C C 2(111). H C C 7 C 9 F 6 C C 7 0.33 C −0.31 . F 8 C C 9, 0.17 0.55 C . I F . 4 C 7 C 9 C ff C 8. B C C C 2(111) C ff C . F ff C - C C C C C C DF ffi - C (∼) . I EB *ab initio*

Table 1 Binding energies of the single Cu atom and the Cu_1–CO complex on adsorption on $CeO_2(111)$ and CeO_2 step as well as key structural parameters. The structures can be seen in Fig. 5

	B	( )	d_{C-} ( )	d_{C-C} ( )
C	111	−2.55	2.03, 2.03, 2.07	—
		−3.92	1.82, 1.83	—
C 1–C	111	−3.05	1.77	1.77
		−3.55	1.91, 2.04	1.80

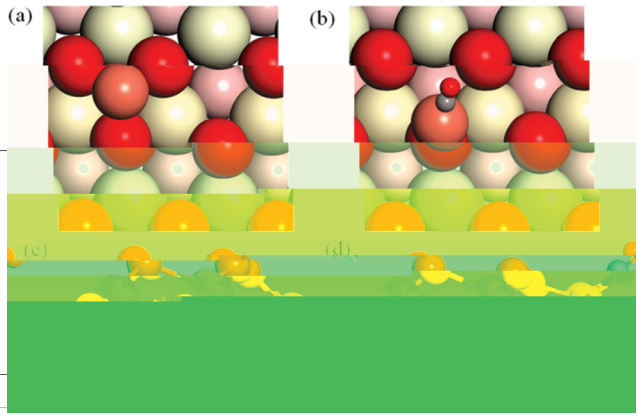

Fig. 5 Optimized structures of a single Cu atom (a and c) and Cu_1–CO complex (b and d) adsorption on $CeO_2(111)$ and a CeO_2 step. Color scheme: Ce, yellow; surface O, red; subsurface O, coral; Cu, bronze; C, grey.

C (−3.69) (F . 2). F
C 1–C −3.55 ,
C 1.91 2.04 .
C C AC –

−2.55 C – 2.04 .
A (1.44) A
C
A -
−1.18 A –
2.18 .[68] A
DF .[32]
I C
C C 2(111). I F . 5 ,
C 1–C
C –
1.77 . I (−3.05
) C ff -
C 2(111)
0.32 (F . 6).
(0.80)
ff A –C C 2(111).[16]

3.4 Trapping at step sites

C . I
(111) .[69] A
A -
[32,39] F
, D *et al.*
[41] I
C C 1–C
[32,39] -
(ML) , 1̄10
C 2· C C –C
F . 5 . F C ,
−3.92 C – -
1.82 1.83 . I

Conflicts of interest

Acknowledgements

F C (21673040), F F (2016J01052), F (C-17055). L E D F M. J K, D C (2017 FA0206500) F C (. 21590802 21733006). H. G. A F ffi (FA9550-18-1-0413) A D

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