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# Synthesis of Co–Sn Intermetallic Nanocatalysts toward Selective Hydrogenation of Citral

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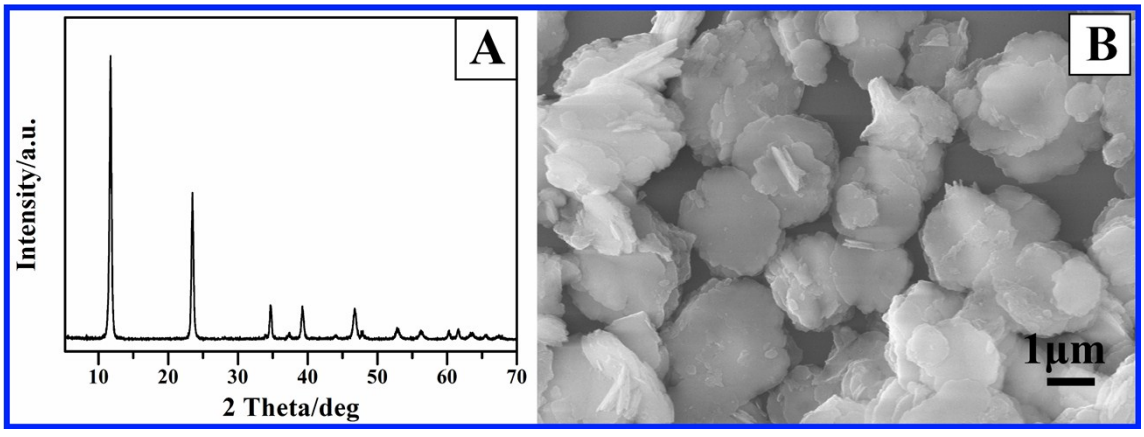


**Fig. S1** (A) XRD pattern and (B) SEM image of the as-synthesized CoZnAl-LDH precursor.

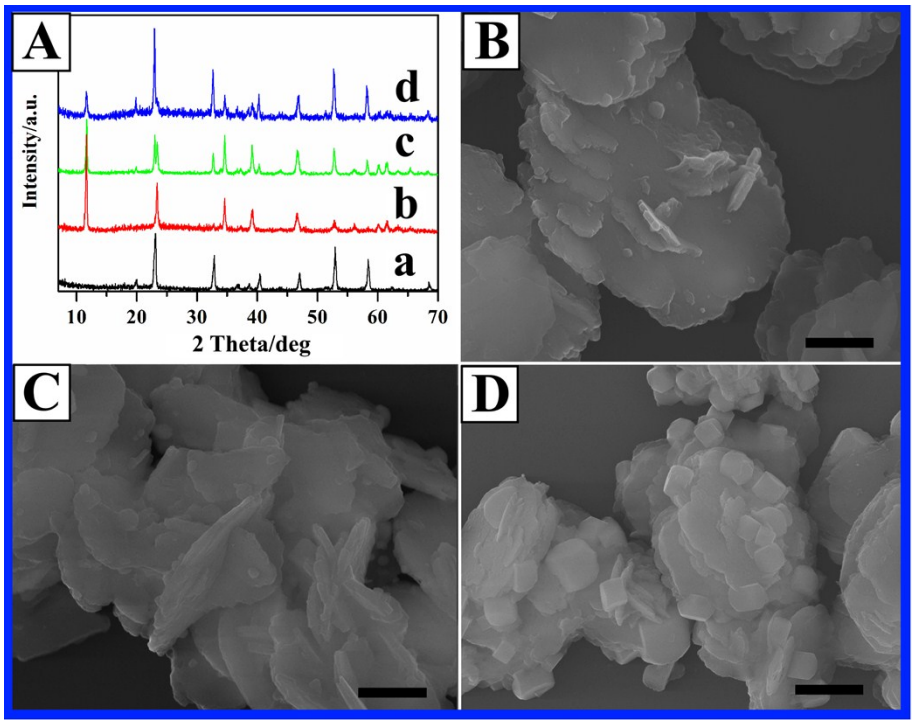


**Fig. S2** (A) XRD patterns of (a) $CoSn(OH)_6$, $CoSn(OH)_6$/CoZnAl-LDHs with Sn/Co molar ratio of (b) 2/2.9, (c) 1/1 and (d) 2/1. SEM images of $CoSn(OH)_6$/CoZnAl-LDHs wih Sn/Co molar ratio of (B) 2/2.9, (C) 1/1 and (D) 2/1. The scale bar is 1 μm.

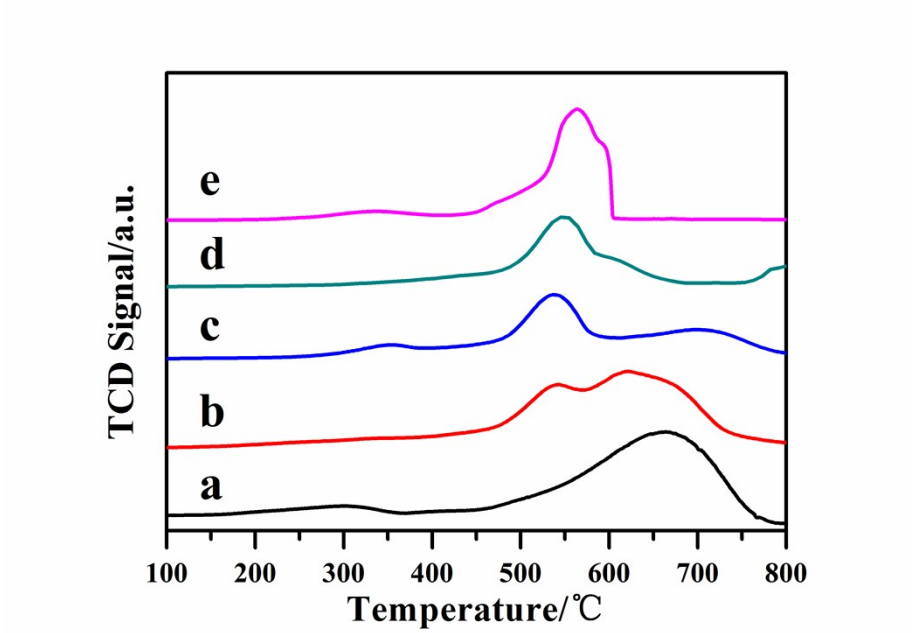


**Fig. S3** $H_2$-TPR profiles for (a) CoZnAl-LDHs, $CoSn(OH)_6$/CoZnAl-LDHs samples with various Sn/Co molar ratio: (b) 2/2.9, (c) 1/1, (d) 2/1, (e) $CoSn(OH)_6$.

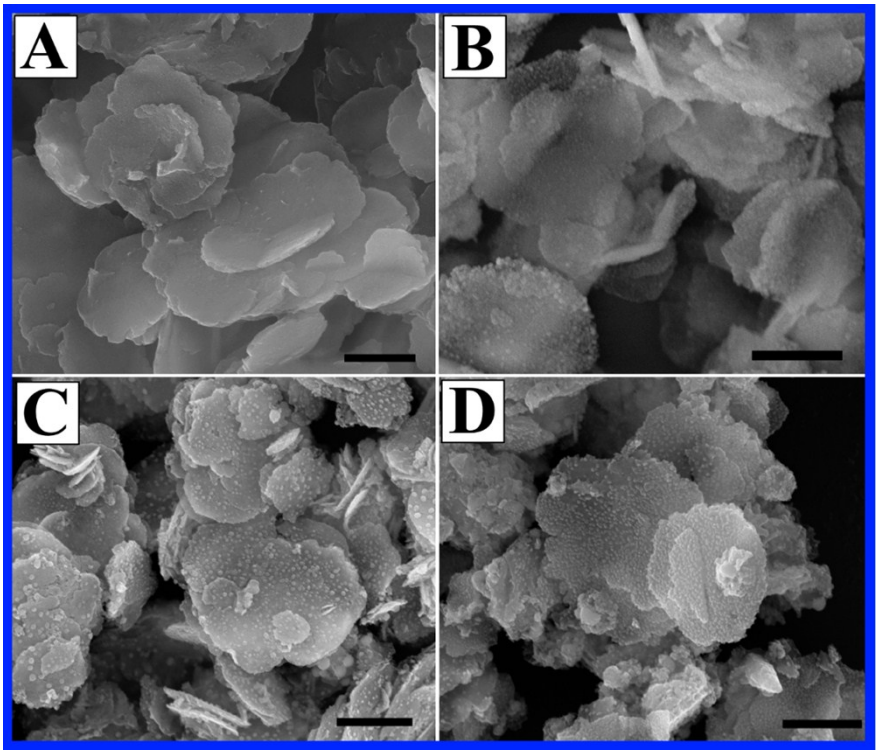


**Fig. S4** SEM images of the as-synthesized supported Co and Co-Sn IMCs in the matrix of ZnO-$Al_2O_3$: (A) Co, (B) $Co_{2.9}Sn_2$, (C) CoSn, and (D) $CoSn_2$. The scale bar is 1 μm.

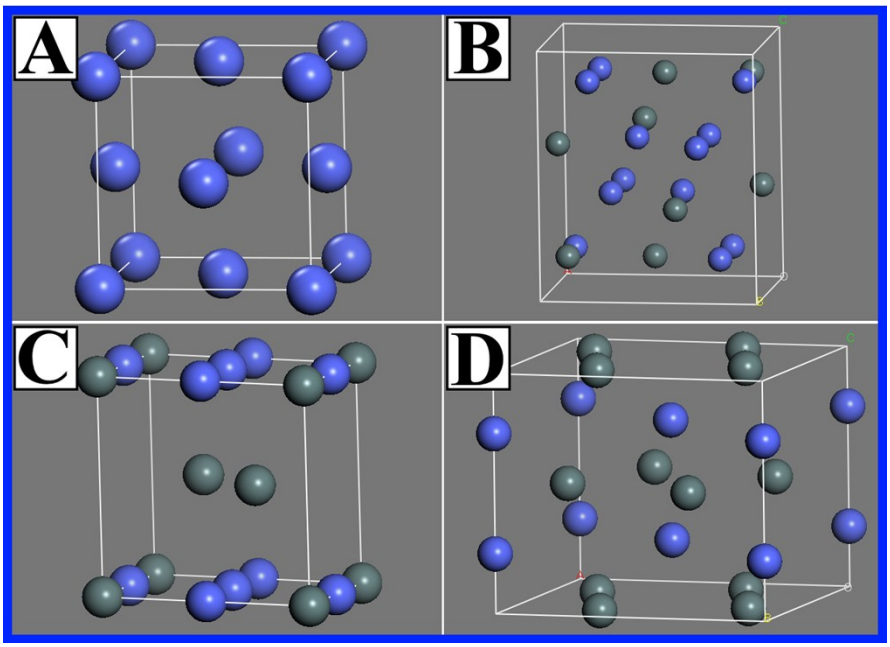


**Fig. S5** Structural models of Co and Co–Sn IMCs: (A) Co, (B) $Co_{2.9}Sn_2$, (C) CoSn, (D) $CoSn_2$. Co: blue ball, Sn: gray ball.

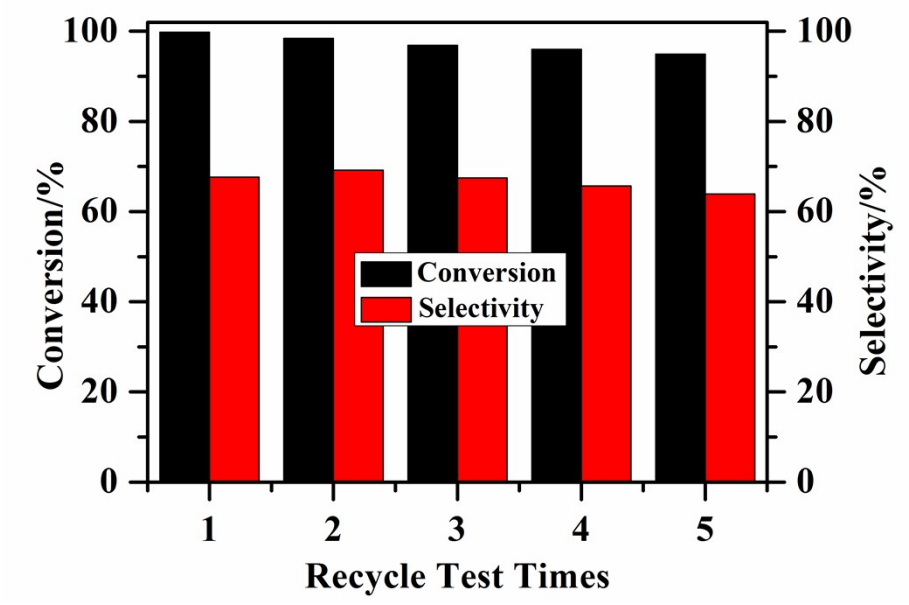


**Fig. S6** Catalyst recycling test over the CoSn IMC catalyst toward citral hydrogenation.

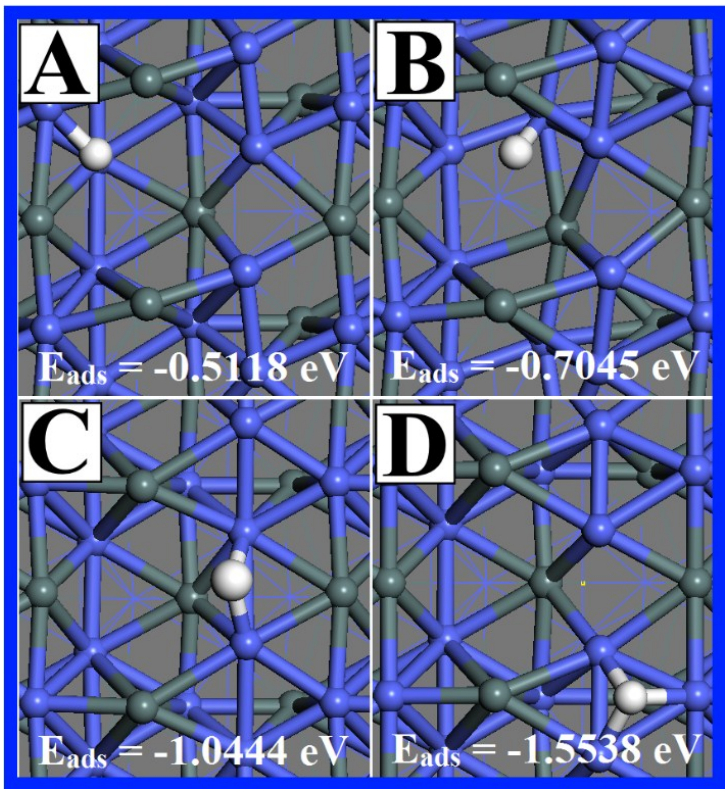


**Fig. S7** Adsorption state of hydrogen on $Co_{2.9}Sn_2$ (004) facet. A, B, C, D correspond to $\alpha$, $\beta$, $\gamma$, $\sigma$ adsorption site in the $H_2$-TPD measurement, respectively.

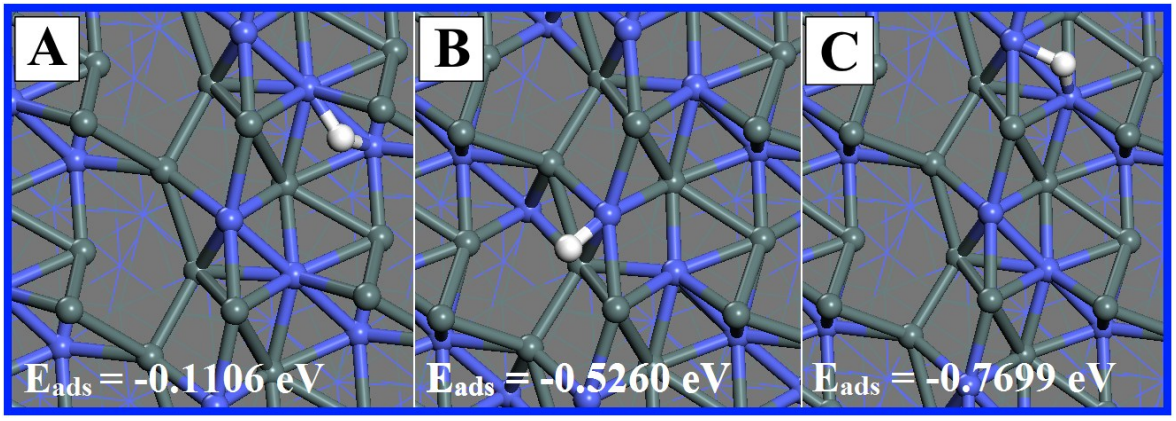


**Fig. S8** Adsorption state of hydrogen on $CoSn_2$ (211) facet. A, B, C correspond to $\alpha$, $\beta$, $\gamma$ adsorption site in the $H_2$-TPD measurement, respectively.

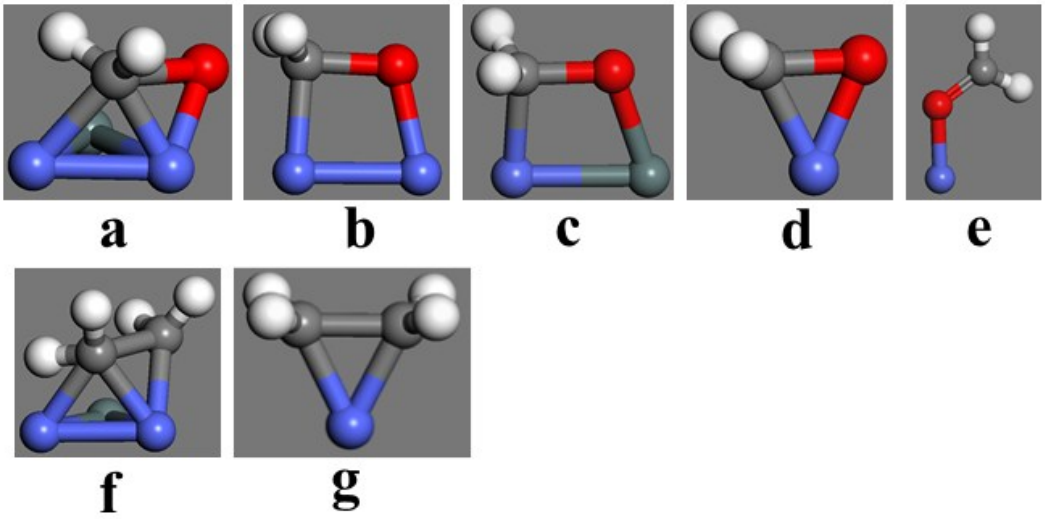


**Fig. S9** Schematic representation for the five adsorption modes of HCHO and two adsorption modes for $C_2H_4$: (a) di-$\sigma_{CO}$l; (b) di-$\sigma_{CO}$; (c) di-$\sigma_{CO}$Sn; (d) $\pi_{CO}$; (e) atop; (f) di-$\sigma_{CC1}$l; (g) $\pi_{CC}$. The blue, dark gray, gray, red and white sphere represent Co, Sn, C, O and H atom, respectively.

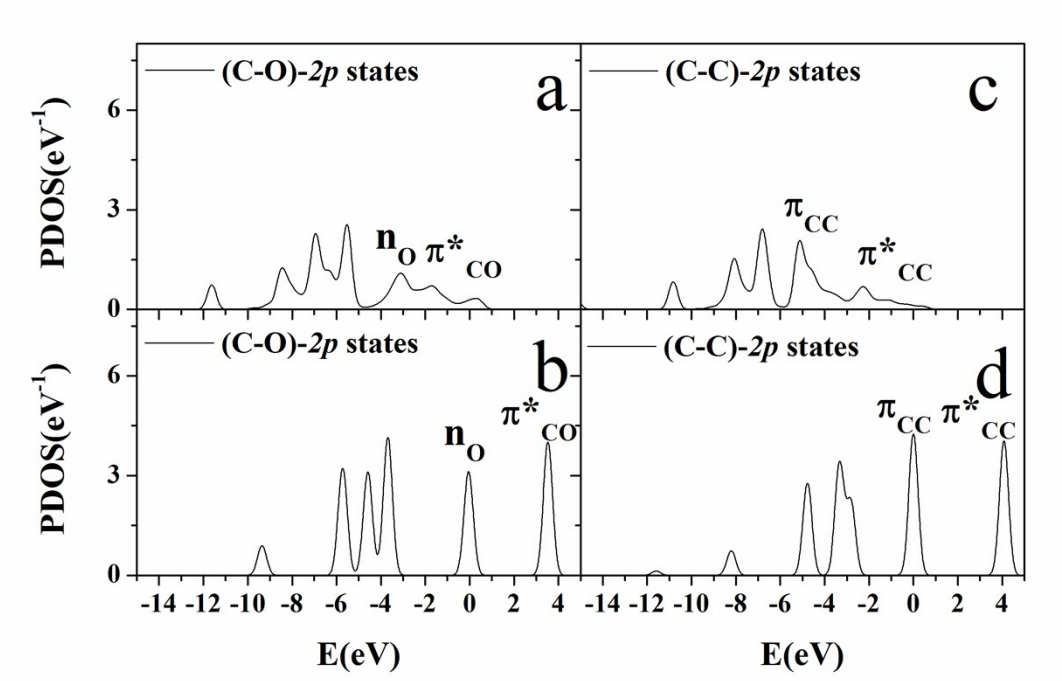


**Fig. S10** Calculated partial densities of states (PDOS) for the adsorbed HCHO and $C_2H_4$ on the mode of (a) di-$\sigma_{CO}$Sn (c) and di-$\sigma_{CC}$l, respectively. The free PDOS for the gas-phase (b) HCHO and (d) $C_2H_4$ are also included for comparison. The Fermi level lies at 0 eV. For free HCHO: the HOMO is $n_O$ at ~0 eV and LUMO is $\pi^*_{CO}$ at ~3 eV. For free $C_2H_4$: the HOMO is $\pi_{CC}$ at ~0 eV and LUMO is $\pi^*_{CC}$ at ~4 eV.

**Table S1.** Adsorption modes, geometrical parameters, charge transfer and adsorption energy for the adsorption of HCHO on the CoSn(201) facet ($L_{CO}$=1.22 Å for free HCHO)

| HCHO | $L_{CoC}$ | $L_{MO}$ | $L_{CO}$ | ∠HCO | Δe [b] | $E_{ads}$ |
|---|---|---|---|---|---|---|
| di-$\sigma_{CO}$l | 2.01/2.13 | 1.90 | 1.33 | 109.3 | 0.2 | −1.75 |
| di-$\sigma_{CO}$ | 1.94 | 1.89 | 1.32 | 111.3 | 0.08 | −1.65 |
| di-$\sigma_{CO}$Sn[a] | 1.90 | 2.33 | 1.29 | 107.2 | 0.08 | −1.13 |
| $\pi_{CO}$ | 2.07 | 1.97 | 1.32 | 115.6 | 0.17 | −0.98 |
| atop | | 1.89 | 1.25 | 119.6 | -0.08 | −0.67 |

[a] The Sn term means that the oxygen atom interacts with a tin atom.

[b] Δe: the charge transfer value from CoSn(201) surface to HCHO.

**Table S2.** Adsorption modes, geometrical parameters, charge transfer and adsorption energy for the adsorption of $C_2H_4$ on the CoSn (201) facet ($L_{CC}$=1.33 Å for free $C_2H_4$)

| $C_2H_4$ | $L_{CoC1}$ | $L_{CoC2}$ | $L_{CC}$ | ∠HCH | Δe [a] | $E_{ads}$ |
|---|---|---|---|---|---|---|
| di-$\sigma_{CC}$l | 2.00/2.05 | 2.00 | 1.44 | 112.9/113.9 | 0.07 | −1.85 |
| $\pi_{CC}$ | 2.06/2.04 | | 1.42 | 115.4/113.4 | 0.08 | −1.34 |

[a] Δe: the charge transfer value from CoSn(201) surface to $C_2H_4$.

**Table S3.** Detailed structural parameters for various catalysts

| Sample | Co content / wt% [a] | Sn content / wt% [a] | Na content / wt% [a] | Specific surface area / ($m^2$ $g^{-1}$) [b] | Mean particle size by TEM / nm | Mean particle size by XRD / nm [c] |
|---|---|---|---|---|---|---|
| Co | 11.3 | 0.0 | 0.0 | 55.6 | 15.3 | 15.1 |
| $Co_{2.9}Sn_2$ | 9.6 | 12.9 | 0.2 | 28.9 | 17.9 | 19.6 |
| CoSn | 9.0 | 18.2 | 0.3 | 34.6 | 19.3 | 21.2 |
| $CoSn_2$ | 7.6 | 30.7 | 0.8 | 15.5 | 20.1 | 22.3 |

[a] Determined by ICP measurement.

[b] Determined by BET measurement.

[c] Determined by Scherrer formula.