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MS-3-P-2558 Co-terminated structure of the spinel Co_3O_4(001) surface confirmed by high-resolution annular dark field scanning transmission electron microscopy.

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Spinel Co3O4 is widely known as an active catalyst of CO oxidation reaction with 100% of conversion rate at -80℃ [1]. This high catalytic activity should be dominated by the interaction between gas molecules [2, 3] (CO, H2O) and Co3O4 surfaces, and it was reported that active Co3+ species should play a key role of the reaction [4]. Therefore the atomic scale investigation of the Co3O4 surface structure is essential to discuss the reaction models.
The Co3O4 (111) surface structure was investigated by LEED, STM and DFT calculations, and a Co-terminated configuration on the oxygen sub-surface layer was proposed as a reasonable structure [5]. However, despite frequently observed facets of the crystal [6], the Co3O4(001) surface has been little discussed. Here, we studied the Co3O4(001) surface by ADF-STEM (annular dark field scanning transmission electron microscopy) imaging (Cs-corrected TEM, TITAN3TM at 300 kV) and confirmed the Co-terminated structure.
The Co3O4(110) specimen was prepared by calcination (1023 K for 12 h in the air) of a thinned CoO(110) wafer (purchased by Crystal Base). In the inset of Fig. 1, the morphology of the specimen is shown by the low magnification image. Clear facets are confirmed as (1-11) and (001) edges, respectively. Fig. 1 shows the ADF-STEM image with atomic resolution, acquired from the square area of the inset, where we can see Co columns of Co3O4 [110]. Some bright spots at the top of the (001) surface were confirmed to have the same atomic periodicity as the Co columns to occupy the oxygen-tetrahedral sites, which means that the Co3O4(001) surface has a Co-terminated structure, similar to the Fe3O4(001) surface [7, 8].
The surface model is summarized in Fig. 2. The top-most Co2+ is located on the oxygen bridge site of the (001) surface. The (1×1) surface unit cell shown in black solid lines in the top view model is composed of one Co2+, two Co3+, and four O2-, which fulfill the stoichiometric surface. Therefore we suggest that the (001) surface is terminated by Co2+, and there is no need of major surface reconstructions such as cation defection or oxygen adatoms. Of course, we should discuss the stability and reactivity of this surface structure, and they will be revealed by the DFT calculations in the future.

[1] Yu, Y. et. al., J. Catal 267 (2009) 121-128
[2] Petitto, A. C. et. al., J. Mol. Catal. A Chemical 281 (2008) 49-58
[3] Xu, X. L. et. al., Surf. Sci. 605 (2011) 1962-1967
[4] Xie, X. et. al., Nature 458 (2009) 746-749
[5] Heinz, K. et. al., J. Phys. Condens. Matter 25 (2013) 173001
[6] Xiao, X. et. al., Adv. Mater. 24 (2012) 5762-5766
[7] Seoighe, C. et. al., Surf. Sci. 440 (1999) 116-124
[8] Rustad, J. R. Surf. Sci. 432 (1999) L583-L588

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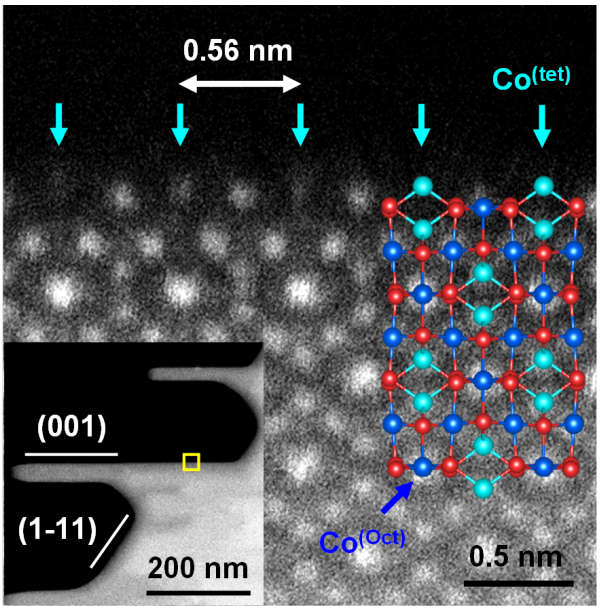

Fig. 1: Fig. 1 ADF-STEM image of Co3O4(001) edge. The color spheres represent O2- (red), Co3+ of oxygen octahedral sites (dark blue) and Co2+ of oxygen tetrahedral sites (light blue). The arrows of light blue color show the atomic column positions of top-most Co2+. The interatomic distance of Co2+-Co2+ is estimated as about 0.56 nm.

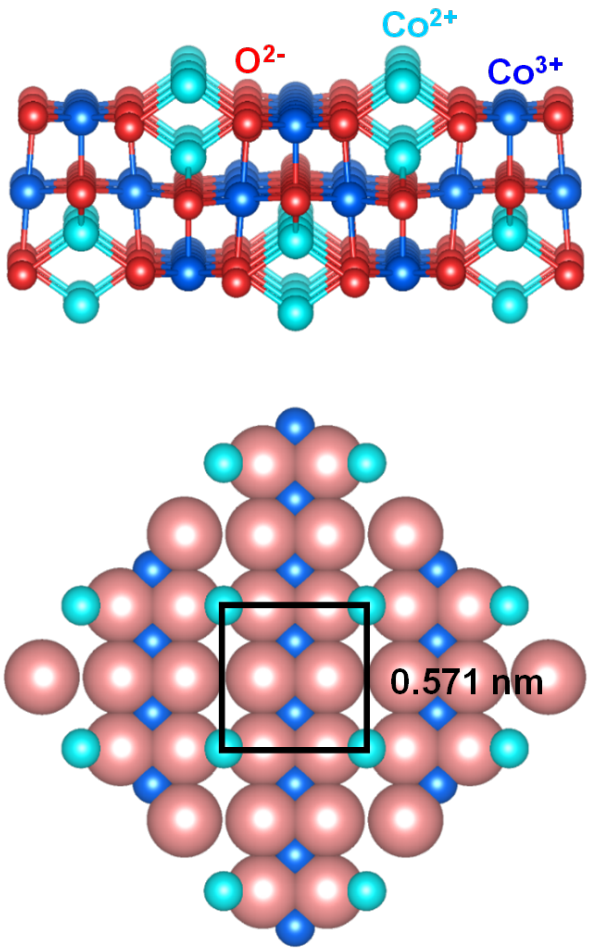

Fig. 2: Fig. 2 Summarized model of the Co3O4(001) surface. The observed atomic distance of top Co2+-Co2+ by ADF-STEM (0.56 nm) is in good agreement with the value of 0.571 nm estimated by the simple crystal model.