Structure-Activity Relationships in Perovskite-Based Materials for Possible TWC Applications

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Introduction

Considerable interest has been created in precious-metal-doped perovskites by reports of a novel self-regeneration process allowing a significant reduction of precious metal usage in TWCs that employ them [1], yet relatively little effort has been expended to carefully probe the nature of the self-regeneration process or establish the fundamental relationships between structure and catalytic activity in these materials. We thus recently used transmission electron microscopy (TEM) to gain new insight into the self-regeneration process [2, 3], and in the present work, we examine some of the structure-activity relationships.

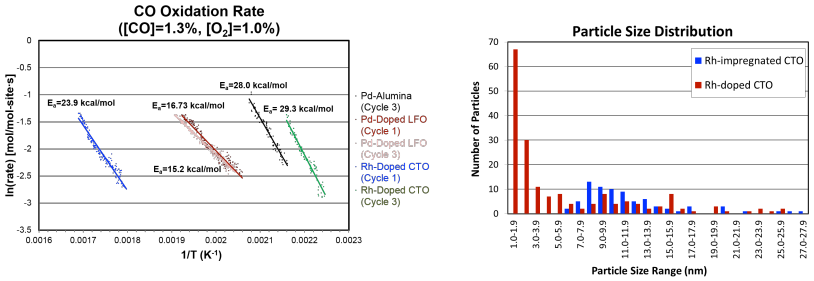
Materials and Methods

High-surface-area (~50 m^2/g) powders of pure and Pd-doped lanthanum iron oxide (LFO) and pure and Rh-doped calcium titanium oxide (CTO) were obtained from Cabot Corporation. The precious metal doping level of each perovskite was nominally 5 % of the B-site cation. Comparable levels of Pd and Rh were loaded onto the surfaces of the pure LFO and CTO powders, respectively, by standard wet impregnation methods, followed by calcination in air. Samples for TEM analysis were aged in a small quartz reactor at 800 °C under a flow of alternating oxidizing (2 % O_2/N_2) or reducing (1 % H_2/N_2) gas, each of 10 min duration, for a total of 3 or 14 h. Samples for catalytic activity measurement were mixed with alumina, pressed into pellets, crumbled and sieved, and then placed into a packed-bed quartz reactor, which was also used for in-situ aging following the same protocol used for the TEM samples.

Results and Discussion

CO oxidation measurements, with $CO:O_2$ ratios ranging from approximately 0.1 to 2.5, suggest that segregation of Pd from Pd-doped LFO is less facile than segregation of Rh from Rh-doped CTO under increasingly reducing conditions, since light-off curves from multiple cycles for Pd were relatively stable, whereas those for Rh evolved on the time scale of the measurements, approaching those of Rh-impregnated CTO. Interestingly, the turn over rate for Pd-doped LFO, where Pd is presumably present as Pd^{2+}, may be comparable to that of Pd/Al_2O_3 at low enough temperature (~160 °C), as shown in Fig. 1(a), due the difference in apparent activation energies.

The likely convergence of the two distinct initial structures in the Rh-CTO system with time in use is more clearly revealed in Fig. 1(b), which shows Rh particle size distributions, measured with TEM, after 14 h of aging. For Rh-doped CTO, there are two distinct modes, one corresponding to an average particle size of order 1 nm in diameter, the other of approximately 10 nm in diameter. The similarity between the size of the larger mode and the average particle size in Rh-impregnated CTO strongly suggests that the larger mode arises from Rh particles that have segregated onto the surface of CTO in the doped material. Though relatively small in number, these particles actually account for more than 90 % of the Rh originally in the doped CTO powder, which maintained much of its original surface area after aging.



(a) (b)

Figure 1. (a) CO oxidation rates for Pd/Al_2O_3, Pd-doped LFO, and Rh-doped CTO containing comparable precious metal levels, normalized by estimated number of Pd^0, Pd^{2+}, and Rh^{2+} surface sites, respectively. (b) Particle size distributions for Rh-doped CTO and Rh-impregnated CTO after 14 h of aging.

Significance

Precious-metal-doped perovskites may exhibit relatively high intrinsic catalytic activities for reactions of interest in TWCs, and most of the precious metal may ultimately be able to segregate onto the surface of the perovskites, if they remain in high-surface-area form, due to the small length scales involved.

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