Investigation of Rh-titanate (ATiO<sub>3</sub>) interactions on high-surface-area perovskites thin films prepared by atomic layer deposition

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## **KEYWORDS**

CO oxidation; Atomic Layer Deposition (ALD); "Intelligent" catalyst; Rh catalyst; CaTiO<sub>3</sub>, SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, perovskites.

## SUPPORTING INFORMATION



**Figure S1.** Growth curves for ALD films on a  $120m^2/g MgAl_2O_4$  support for ( $\Delta$ ) Sr-ALD process and ( $\Box$ ) Ba-ALD process



**Figure S2.** Growth curves for ALD films on a  $120m^2/g MgAl_2O_4$  support for (•) SrTiO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> and (•) BaTiO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> process.

**Table S2.** Results from Rietveld analysis of the XRD patterns of the  $CaTiO_3/MgAl_2O_4$  after high temperature redox cycles, in comparison with the cell parameters reported for the parent pure phases.

	CaTiO <sub>3</sub> /MgAl <sub>2</sub> O <sub>4</sub>		Parent pure phase
Phase (Space Group)	Amount (wt%)	Cell parameters (nm)	Cell parameters (nm)
MgAl <sub>2</sub> O <sub>4</sub> (Fd <sup>3</sup> m)	76.5%	a = 0.8008	a = 0.8081
CaTiO <sub>3</sub> (Pnma)	23.5%	a = 0.5435 b = 0.7662 c = 0.5389	a = 0.5442 b = 0.7640 c = 0.5380



Figure S3. Rietveld refinement for the CaTiO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> samples.



**Figure S4.** STEM result for  $Rh/MgAl_2O_4$ , after five 1073-K redox cycles, with the final step being reduction.



**Figure S5.** FTIR patterns obtained for (a)  $Rh/CaO/MgAl_2O_4$  and (b)  $Rh/TiO_2/MgAl_2O_4$  after exposure to CO at room temperature after five 1073 K redox cycles with the final treatment being reduction.



**Figure S6.** Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr  $O_2$  for Rh/CaTiO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> with extra Ca (Ca:Ti=1.1) as a function of reduction temperature. Reduction pretreatment temperature: (white) no reduction, (grey) 573 K reduction, and (black) 1073 K reduction.



**Figure S7.** Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr  $O_2$  for (a) Rh/CaO/MgAl<sub>2</sub>O<sub>4</sub> (b) Rh/TiO<sub>2</sub>/MgAl<sub>2</sub>O<sub>4</sub> as a function of reduction temperature. Reduction pretreatment temperature: (white) no reduction, (grey) 573K reduction and (black) 1073K reduction.



Figure S8. CO-TPR profile for (a)Rh/CaO/MgAl<sub>2</sub>O<sub>4</sub> and (b)Rh/TiO<sub>2</sub>/MgAl<sub>2</sub>O<sub>4</sub>