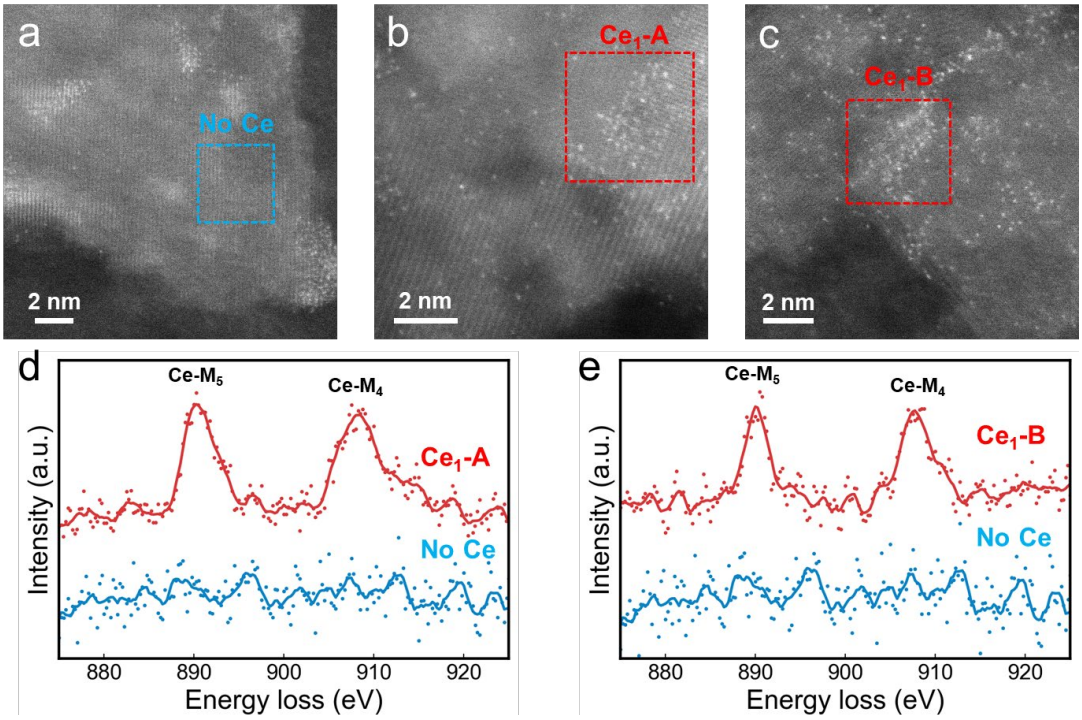
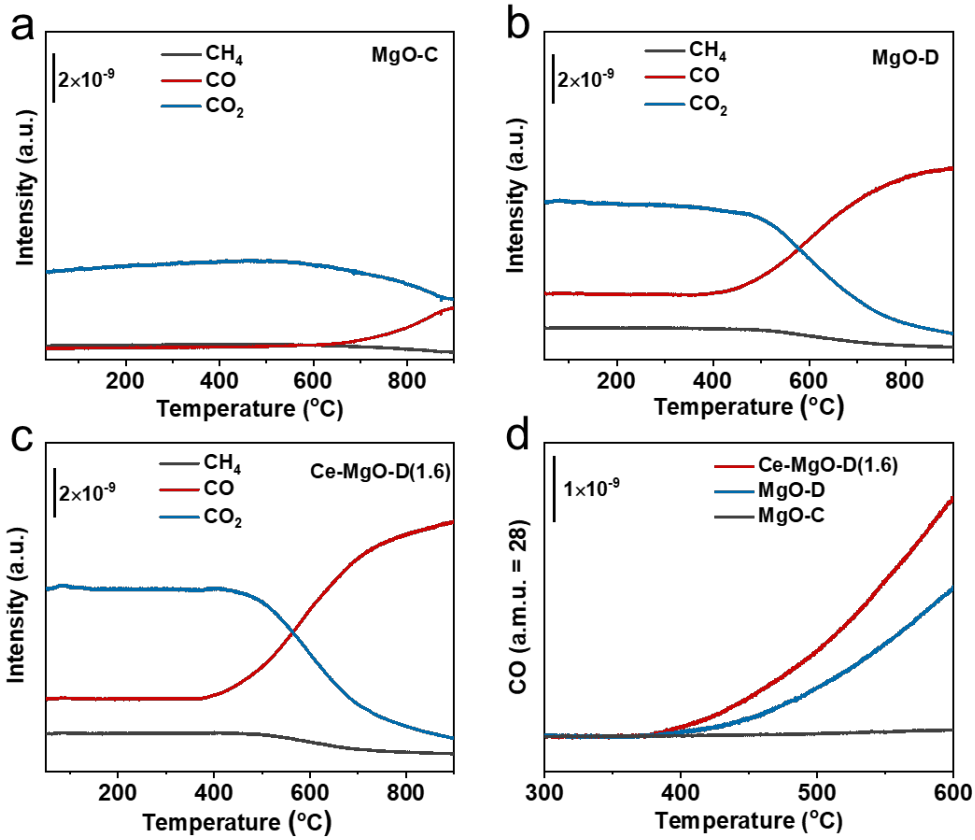
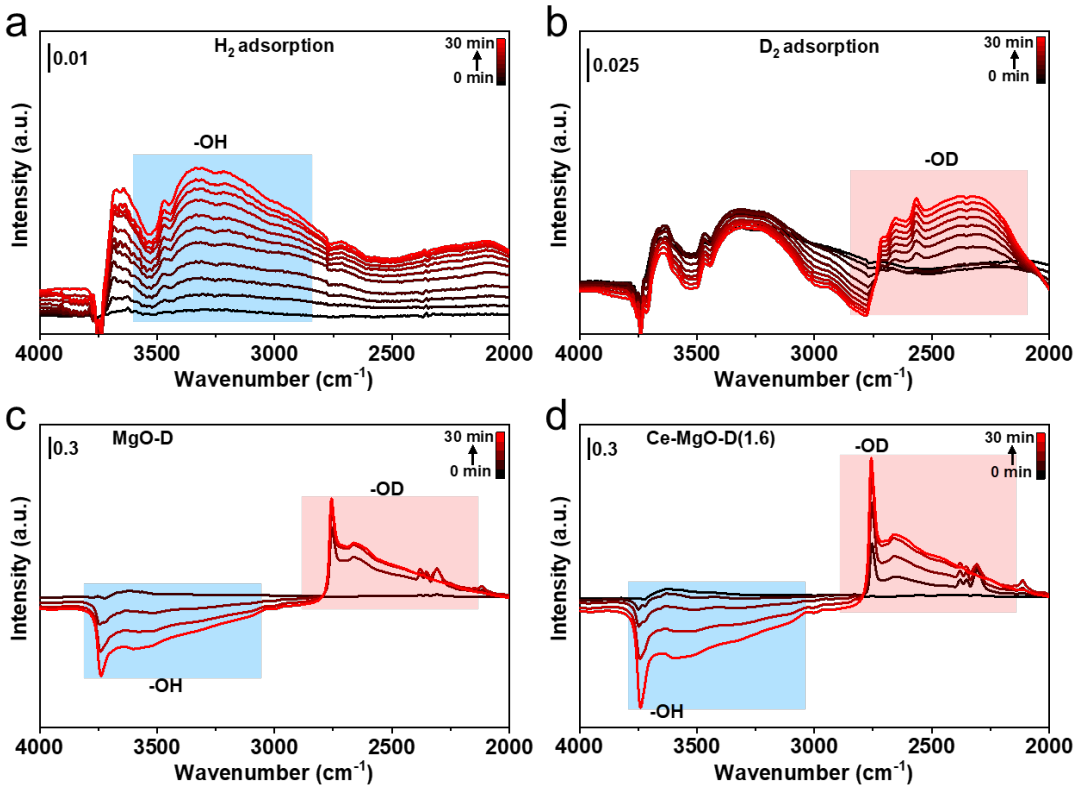
EXTENDED DATA



Extended Data Figure 1 | Microscopy characterizations of Ce-MgO-D(1.6). (a-c) Atomic resolution STEM-ADF images of Ce-MgO-D(1.6) catalyst and the corresponding regions of STEM-EELS. Three representative regions were selected for Ce-MgO-D(1.6) catalyst: blue square on the MgO without Ce atom (No Ce), red square on the MgO with Ce atom (Ce_1-A, and Ce_1-B). (**d, e)** EELS spectra of marked regions for Ce-MgO-D(1.6) in **a**, **b** and **c**, respectively.



Extended Data Fig. 2 | Surface evolution reaction. a-c, CO_2-TPSR profiles of MgO-C **(a)**, MgO-D **(b)** and Ce-MgO-D(1.6) **(c)** catalysts. **d,** Mass spectral (MS) signals of CO (m/z = 28) in TPSR experiments for the MgO-C, MgO-D and Ce-MgO-D(1.6) catalysts. From the profile for the formation of carbon monoxide during TPSR, a lower onset temperature over Ce-MgO-D(1.6) catalyst was found. Meanwhile, the CO formation rate of Ce-MgO-D(1.6) was higher than the pure MgO-D and MgO-C catalysts, indicating the Ce-MgO-D(1.6) has much higher activity in the RWGS reaction.



Extended Data Fig. 3 | H-D isotopic exchange DRIFT spectra. In situ DRIFTS spectra of the Ce-MgO-D(1.6) treated with **a)** H_2 and **b)** D_2 at room temperature. The sample was first reduced at 500 °C in H_2 and then switched to Ar, the background spectrum was collected at room temperature in Ar. Ce-MgO-D(1.6) show an enhanced number of hydroxy group (-OH, the wide infrared band between 3600-2800 cm^{-1}) during H_2 flow. Similarly, the increased number of -OD group was observed when Ce-MgO-D(1.6) exposed to D_2 flow. **c, d,** In situ H-D isotope exchange DRIFTS spectra of MgO-D **c)** and Ce-MgO-D(1.6) **d)** exposed D_2 at 450 °C. Upon treatment with D_2, the negative bands at 3200-3790 cm^{-1} and the positive bands at 2380-2800 cm^{-1} appeared simultaneously, displaying the expected H-D isotopic exchange for the MgO-H bands. Ce-MgO-D(1.6) catalyst shows significantly improved H-D exchange activity compared with MgO-D, confirming the enhanced hydrogen dissociation activity. The improved oxygen defects in Ce-MgO-D(1.6) increases the active H* which may react with CO_2 to form formate species.