Electronic supporting Information

Spectroscopic Investigation on the Structural Transformation of Ru in the Ru/CeO_2 Catalyst

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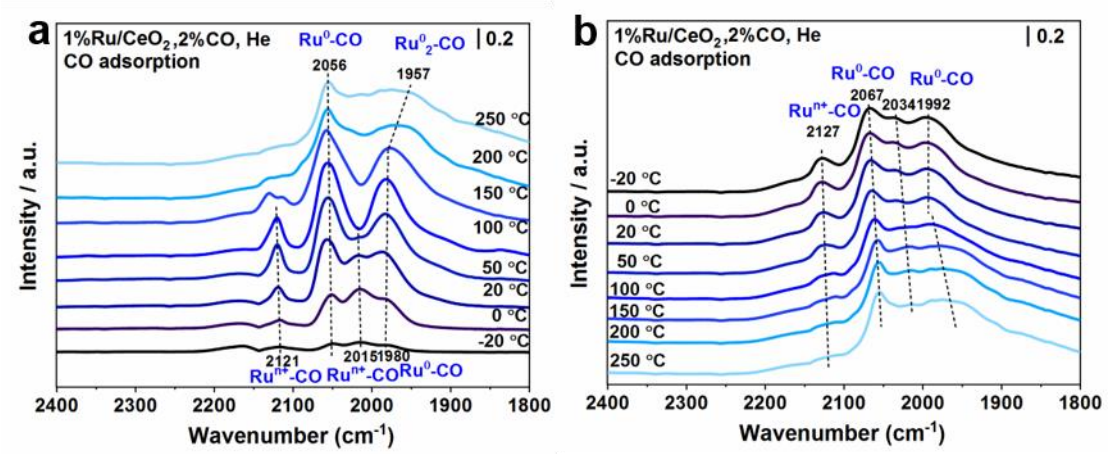

Fig. S1 *In situ* DRIFTS results of Ru/CeO_2 catalyst after pretreatment in O_2: (a) CO adsorption results during heating process (−20 °C to 250 °C); (b) CO adsorption results during cooling process (250 °C to −20 °C)

The CO adsorption on Ru species was very complex, which included monocarbonyl, dicarbonyl, and tricarbonyl species adsorbed on Ru sites with different oxidation states. The positions of the bands were likely to have been red-shifted as the temperature increased because of the decrease in surface coverage that led to a weaker dipole-dipole coupling.

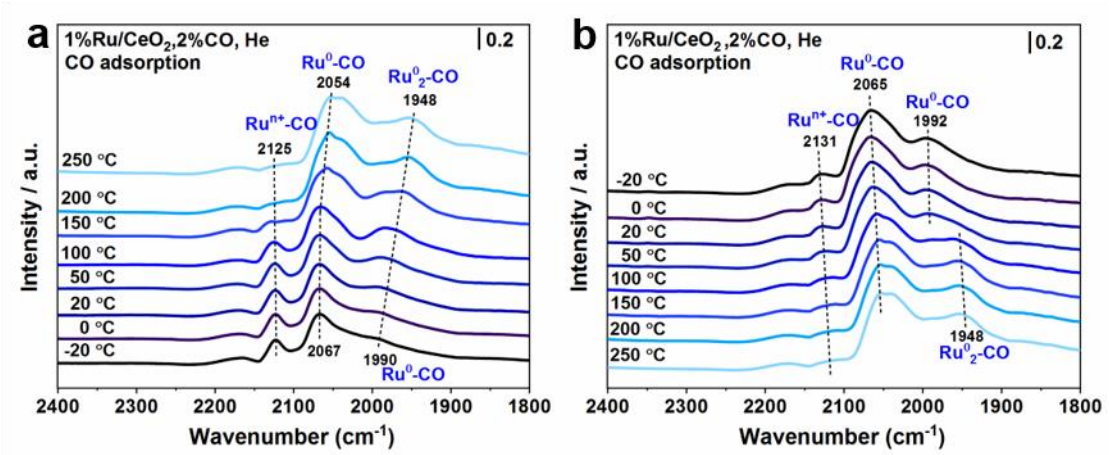

Fig. S2 *In situ* DRIFTS results of Ru/CeO_2 catalyst after pretreatment in H_2-N_2: (a) CO adsorption results during heating process (−20 °C to 250 °C); (b) CO adsorption results during cooling process (250 °C to −20 °C)

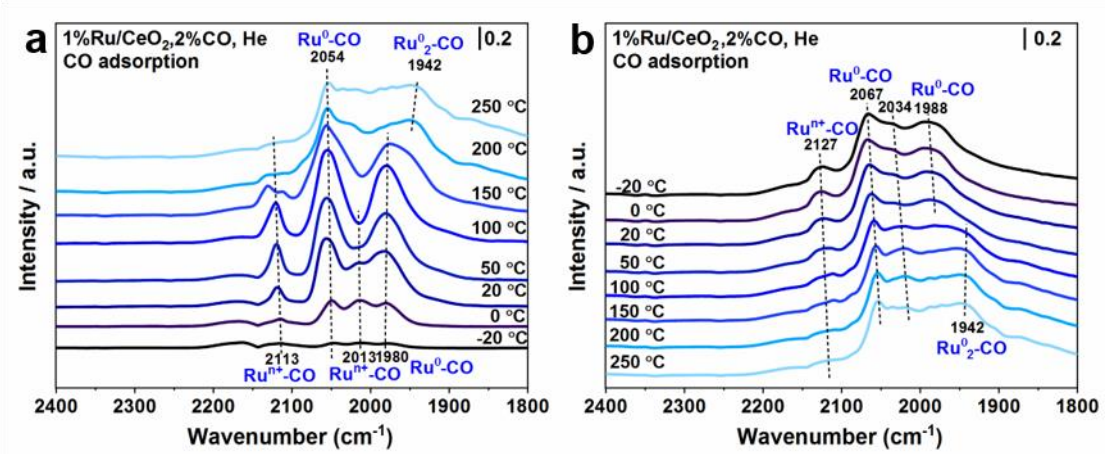

Fig. S3 *In situ* DRIFTS results of Ru/CeO_2 catalyst after pretreatment in H_2-O_2: (a) CO adsorption results during heating process (−20 °C to 250 °C); (b) CO adsorption results during cooling process (250 °C to −20 °C)

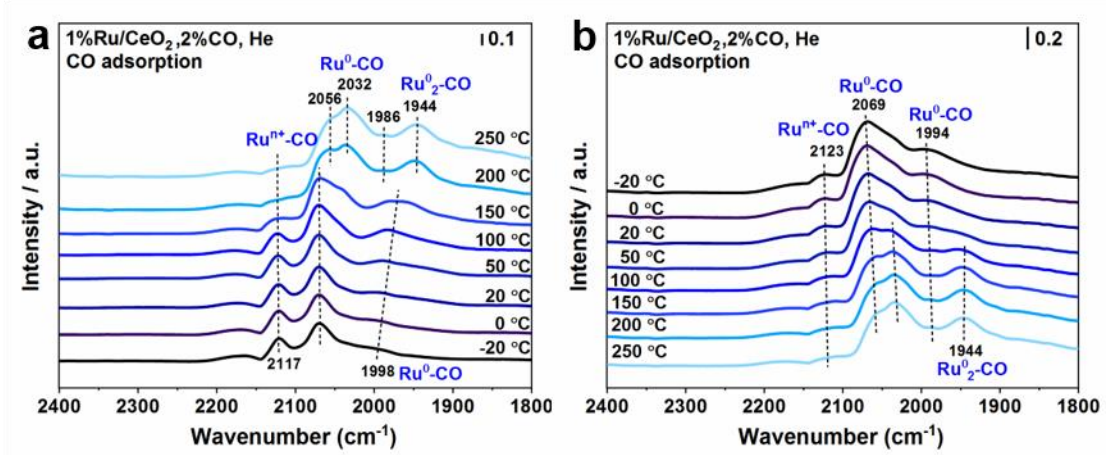

Fig. S4 *In situ* DRIFTS results of Ru/CeO_2 catalyst after pretreatment in N_2: (a) CO adsorption results during heating process (−20 °C to 250 °C); (b) CO adsorption results during cooling process (250 °C to −20 °C)

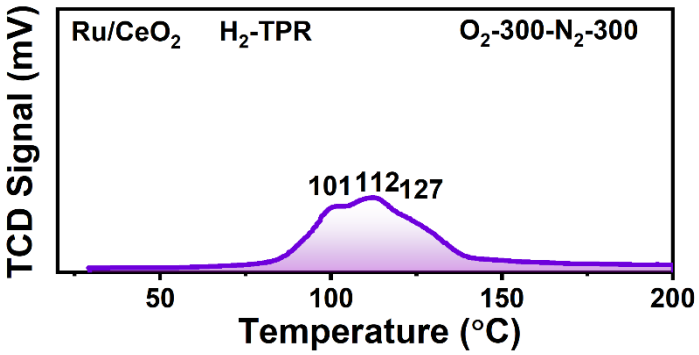

Fig. S5 The H_2-TPR of the Ru/CeO_2 catalyst after pretreatment in O_2-N_2 atmospheres

It showed an overall broad peak around 110 °C, which was considered as the reduction of RuO_x clusters. This phenomenon indicated that although N_2 was an inert gas, it could still cause state changes of Ru species at a high temperature. Besides, we also found that after treated with N_2 atmosphere at 300 °C, the well-dispersed Ru single atoms gradually agglomerated into Ru nanoclusters and the state of Ru species changed significantly.

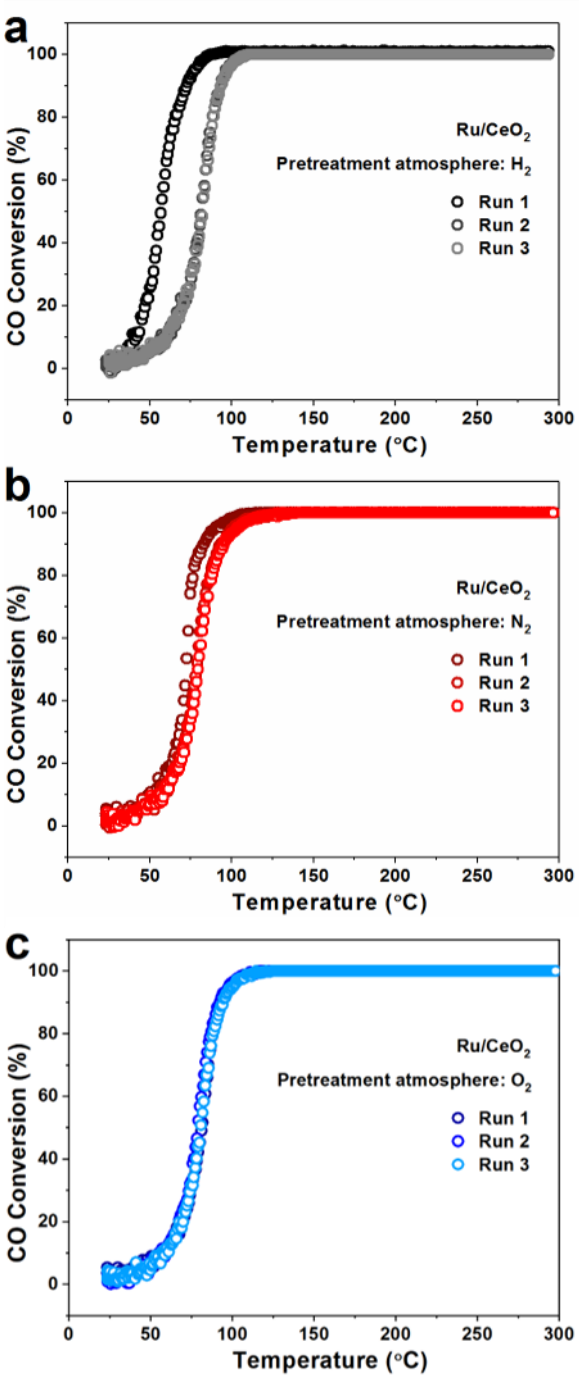

Fig. S6 Three rounds CO oxidation activity results of Ru/CeO_2 catalyst after pretreatment in H_2, N_2 and 20% O_2/N_2: (a) 5% H_2/Ar; (b) N_2; (c) 20% O_2/N_2

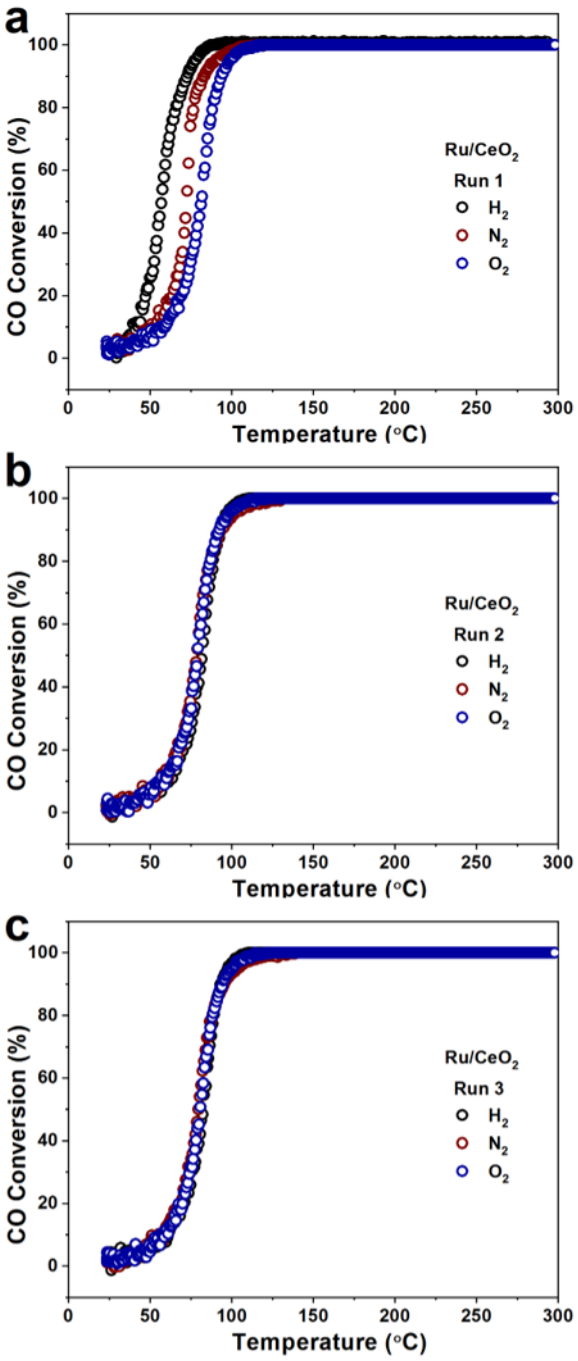

Fig S7. Three rounds CO oxidation activity results of Ru/CeO_2 catalyst after pretreatment in 5% H_2/Ar, N_2 and 20% O_2/N_2: (a) the result of the first-round of testing; (b) the result of the second-round of testing; (c) the result of the third-round of testing

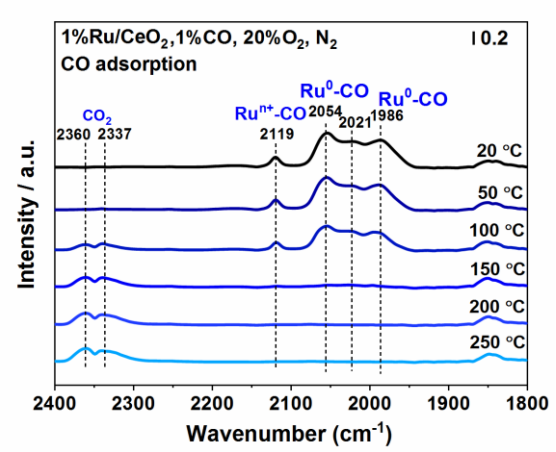

Fig. S8 *In situ* DRIFTS results of Ru/CeO_2 catalyst in CO oxidation reaction gas after pretreatment in 20% O_2/N_2 during cooling process (250 °C to 20 °C)

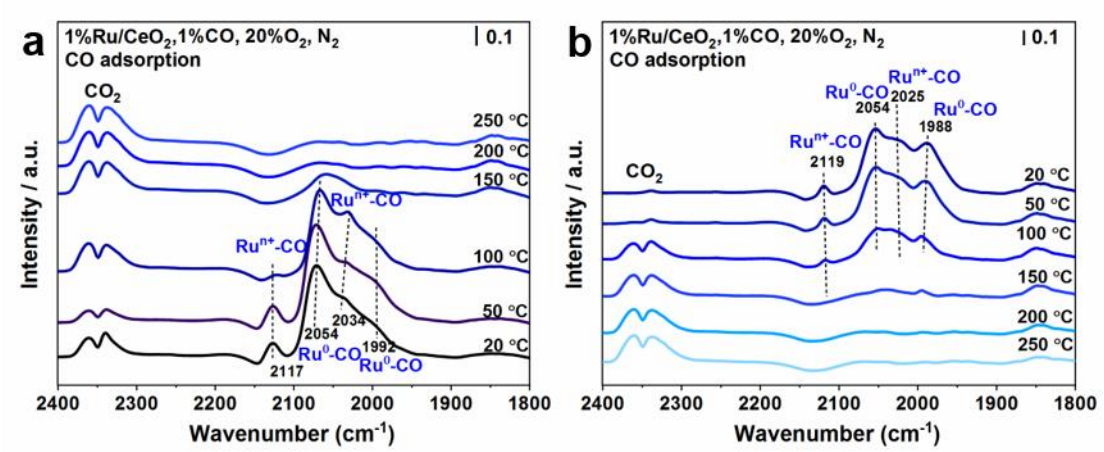

Fig. S9 *In situ* DRIFTS results of Ru/CeO_2 catalyst in CO oxidation reaction gas after pretreatment in H_2: (a) the test results during heating process (20 °C to 250 °C); (b) the test results during cooling process (250 °C to 20 °C)

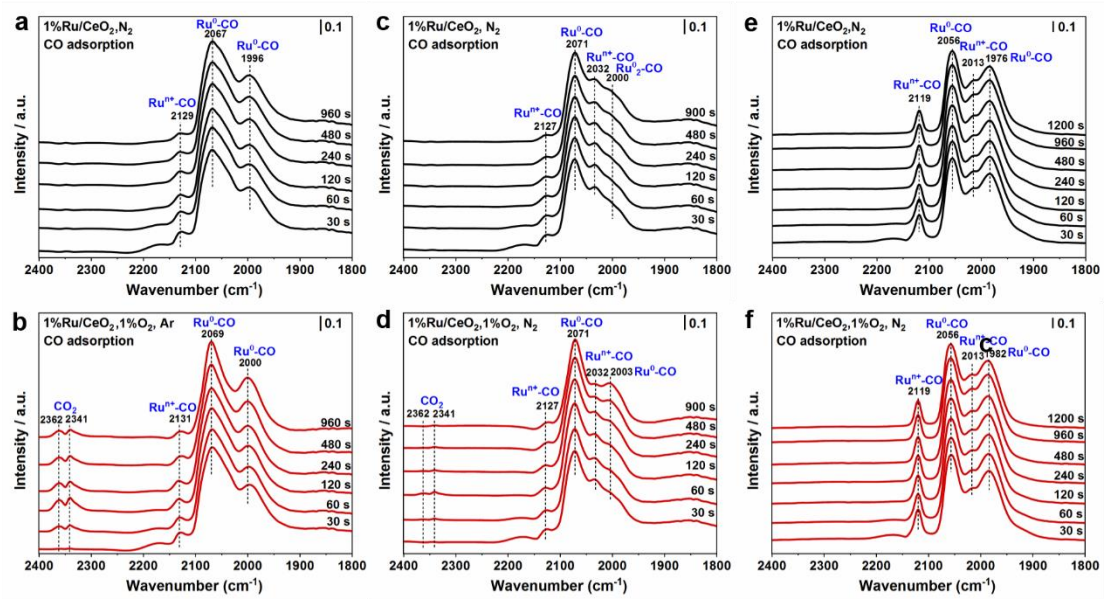

Fig. S10 *In situ* DRIFTS study of CO adsorption on the Ru/CeO_2 catalysts after pretreatment ((a, b) H_2, (c, d) N_2, (e, f) air, 300 °C) at 20 °C: (a, c, e) N_2 purging, (b, d, f) 1% O_2/Ar purging

The *in situ* DRIFTS in a "CO-N_2–CO-O_2" mode was performed to explore the active Ru site for CO oxidation reaction. However, the CO adsorption on Ru site showed no obvious difference at 20 °C. The reason for the result might attribute to the low activity of the Ru/CeO_2 for CO oxidation under this condition.

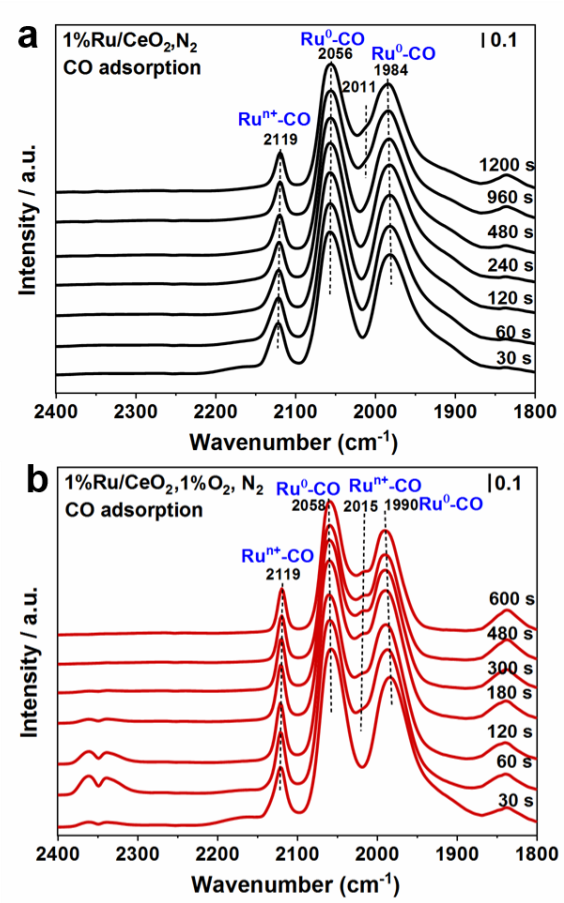

Fig. S11. *In situ* DRIFTS study of CO adsorption on the Ru/CeO_2 catalysts after pretreatment (O_2, 300 °C) at 100 °C: (a) N_2 purging, (b) O_2 purging

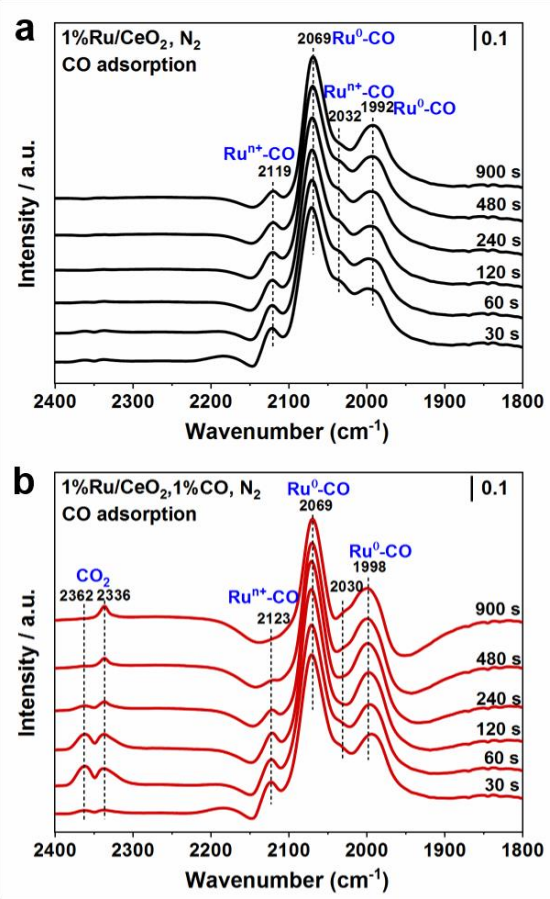

Fig. S12. *In situ* DRIFTS study of CO adsorption on the Ru/CeO_2 catalysts after pretreatment (N_2, 300 °C) at 100 °C: (a) N_2 purging, (b) O_2 purging