

Supporting Information for:

**Mechanistic aspects of deNO_x processing over
TiO₂ supported Co-Mn oxide catalysts:
structure-activity relationships and *in situ*
DRIFTS analysis**

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Catalyst Preparation. The Co/TiO₂ catalyst with the same Co content in Co(3)-Mn/TiO₂ was prepared by a conventional impregnation method. Anatase TiO₂ and precursor salt Co(CH₃COO)₂ 4H₂O were purchased from Sinopharm Chemical Reagent Company and used without further purification. In a typical synthesis, 20 mL of the aqueous precursor solution of Co(CH₃COO)₂ was added into a 50 mL beaker containing 2.0 g TiO₂. The mixture was stirred for 3 h, dried at 80 °C for 18 h and then calcined at 500 °C for 2 h to get the Co/TiO₂ catalyst.

Table S1. Specific Surface Area and Pore Volume of Co/TiO₂ Catalyst

catalyst	surface area (m ² g ⁻¹)	pore volume (cm ³ g ⁻¹)
Co/TiO ₂	47.1	0.20

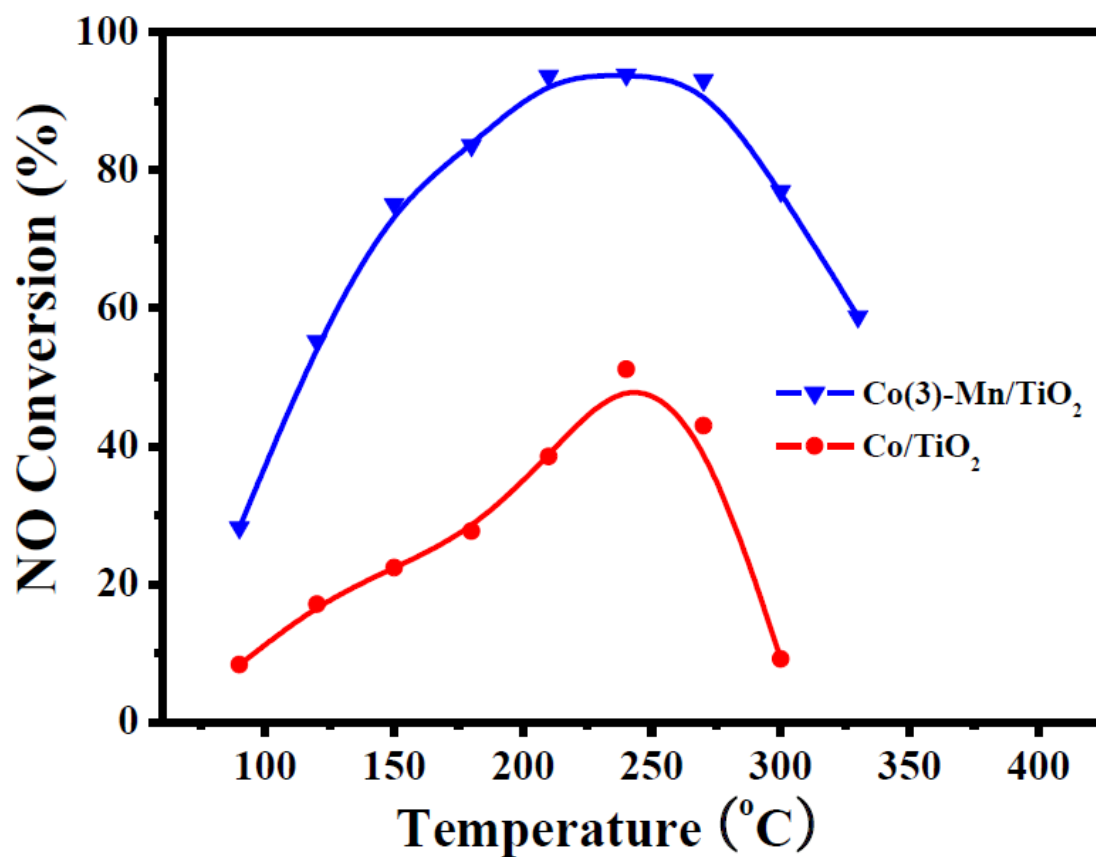


Figure S1. NO_x conversion during the NH₃-SCR reaction over Co(3)-Mn/TiO₂ and Co/TiO₂ catalysts. Reaction conditions: 500 ppm NO, 500 ppm NH₃, 5 vol% O₂, N₂ as balance gas, total flow rate 270 mL/min and GHSV= 40 000 h⁻¹.

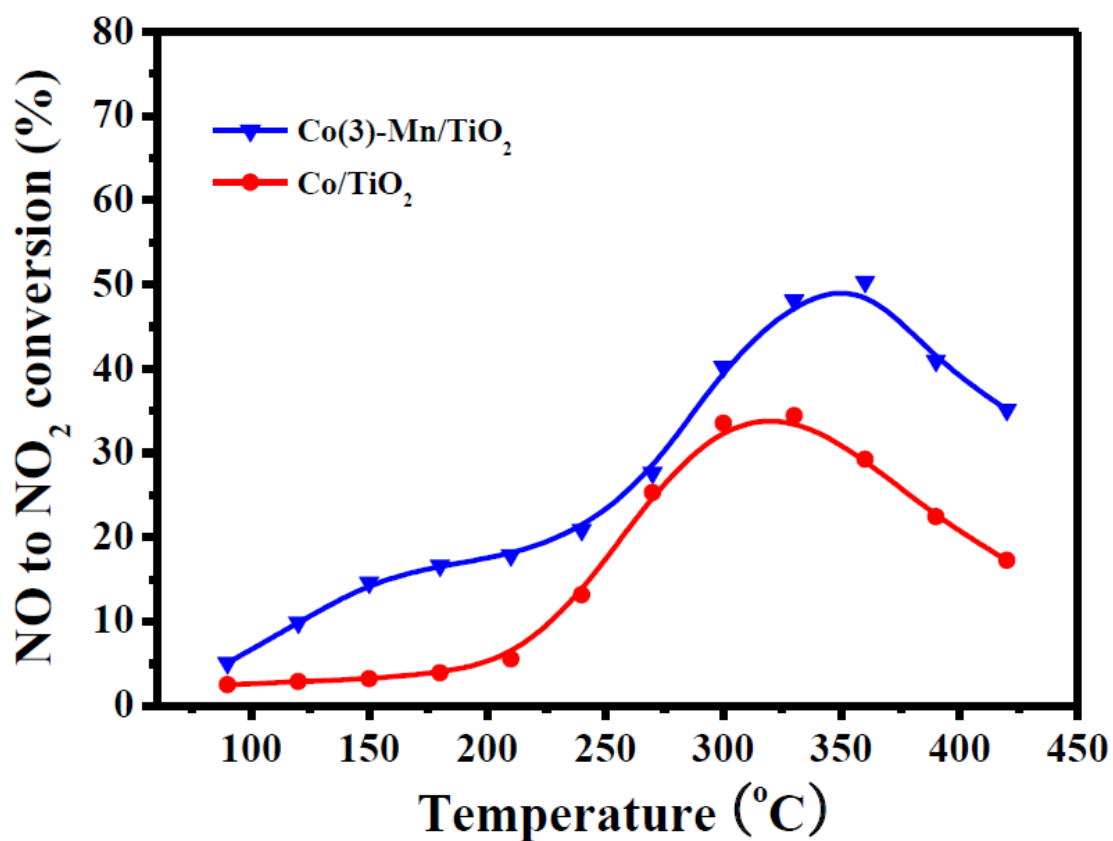


Figure S2. NO to NO₂ conversion during the NO oxidation reaction over Co(3)-Mn/TiO₂ and Co/TiO₂ catalysts. Reaction conditions: 500 ppm NO, 5 vol% O₂, N₂ as balance gas, total flow rate 270 mL/min and GHSV= 40 000 h⁻¹.

It can be seen that Co/TiO₂ catalyst hardly exhibits NO oxidation ability in low-temperature range, which is corresponding to the poor low-temperature catalytic activity.

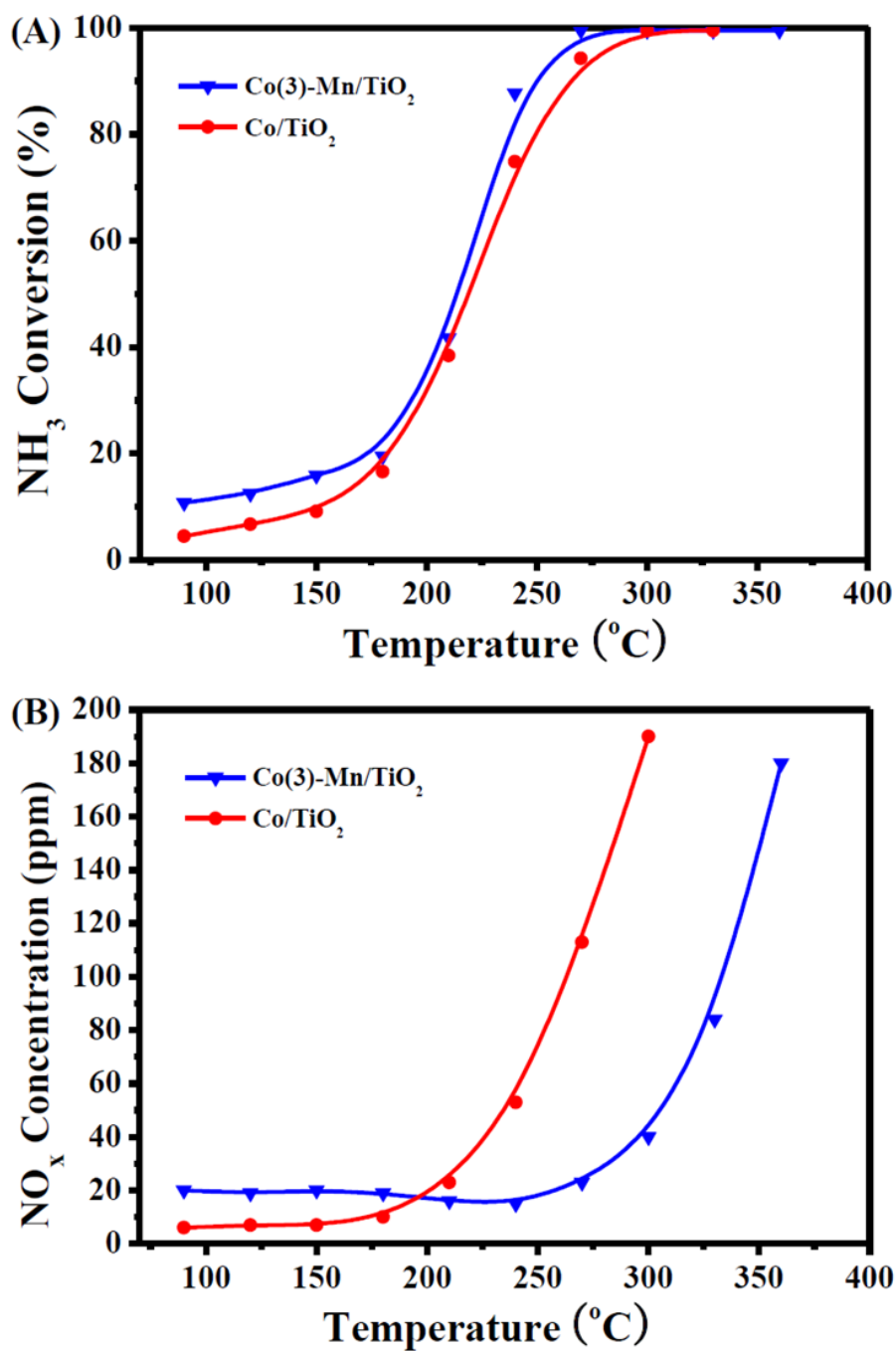


Figure S3. (A) NH₃ conversion and (B) NO_x concentration during the NH₃ oxidation reaction over Co(3)-Mn/TiO₂ and Co/TiO₂ catalysts. Reaction conditions: 500 ppm NH₃, 5 vol% O₂, N₂ as balance gas, total flow rate 270 mL/min and GHSV= 40 000 h⁻¹.

The NH₃ oxidation ability of Co/TiO₂ is about the same to that of Co(3)-Mn/TiO₂, but the unselective NH₃ oxidation ability is much stronger (Figure S3B).

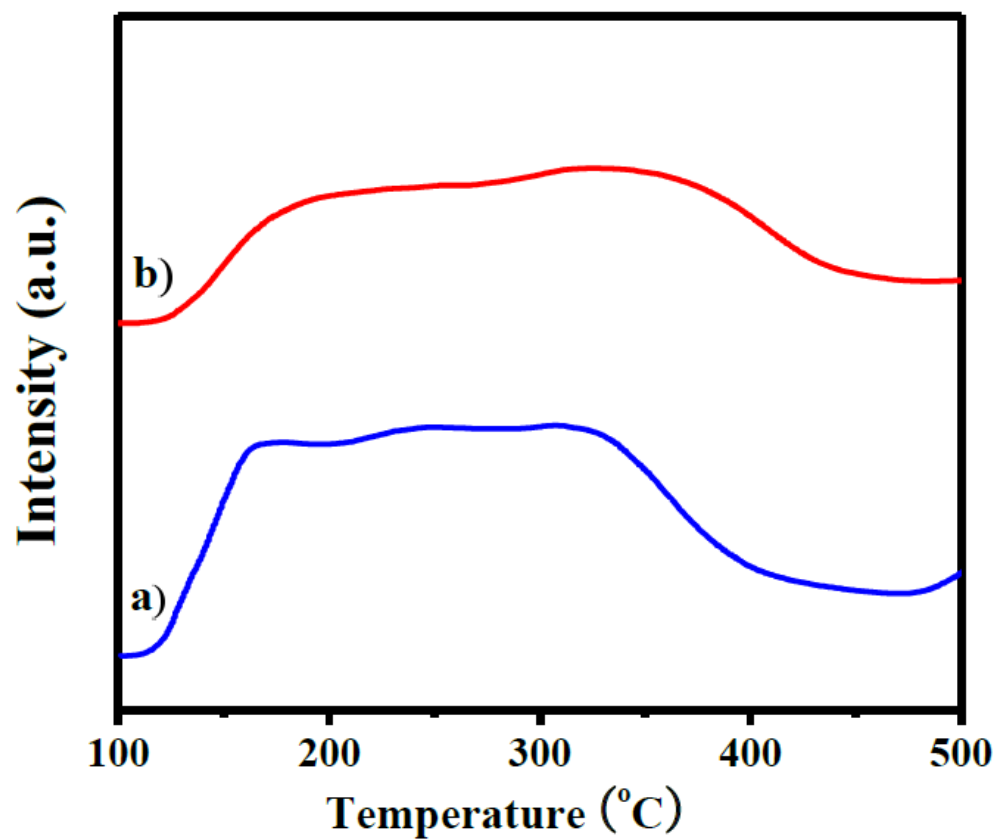


Figure S4. NH₃-TPD profiles of the catalysts: (a) Co(3)-Mn/TiO₂ and (b) Co/TiO₂.

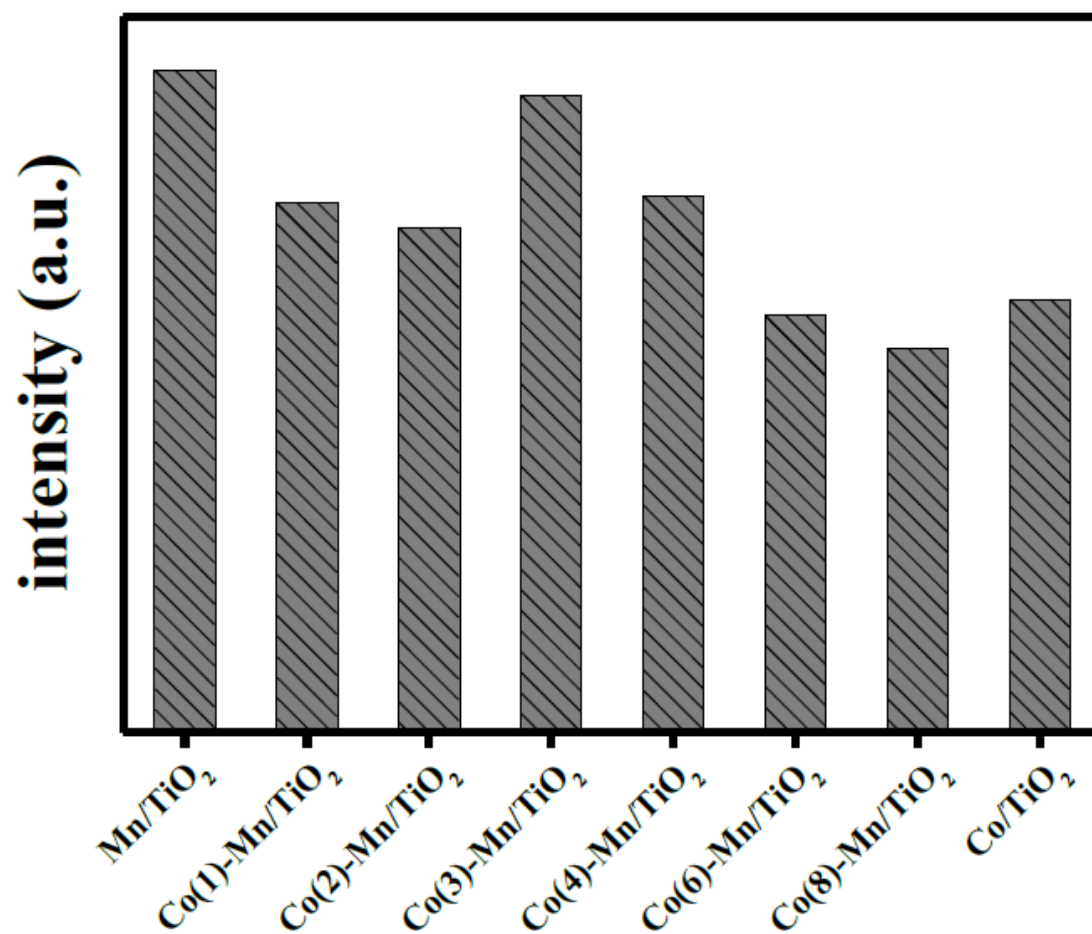


Figure S5. Relative amount of the surface acid sites based on NH₃-TPD results.

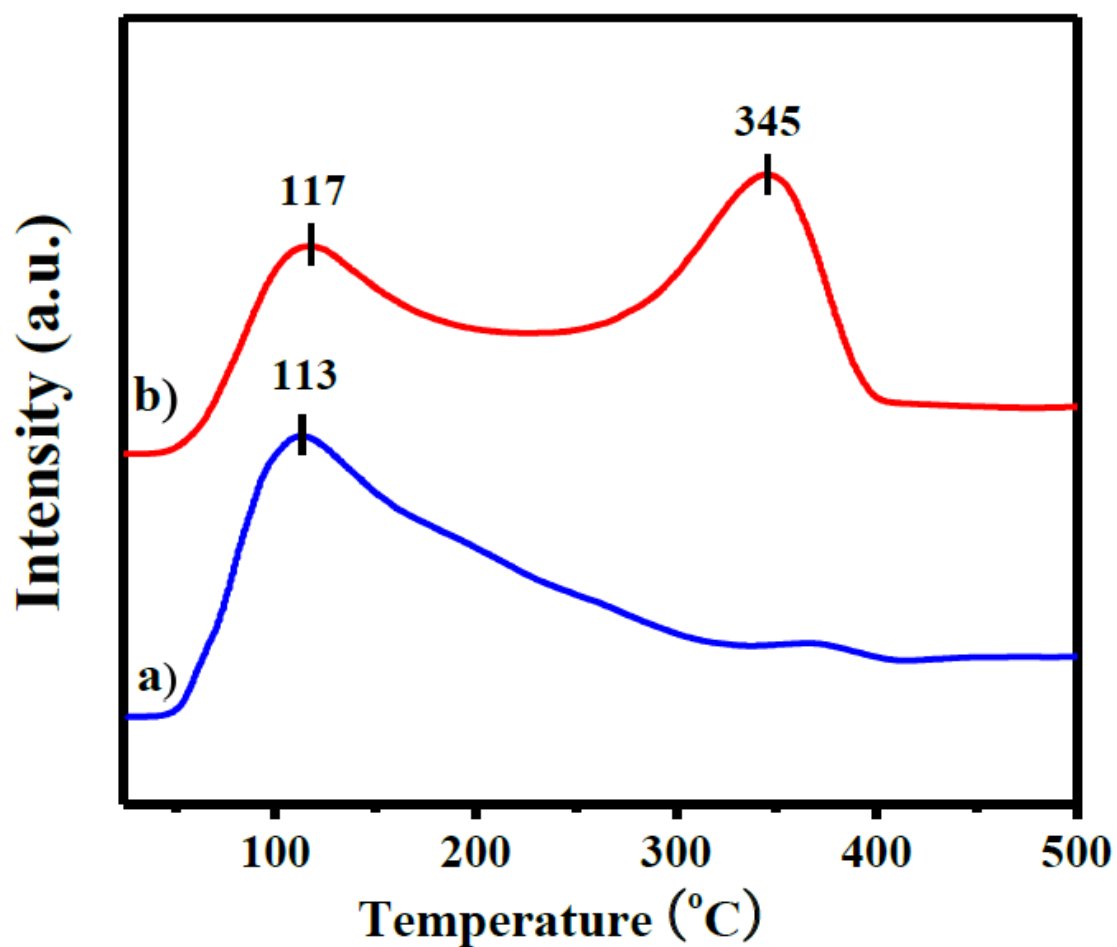


Figure S6. NO_x-TPD profiles of the catalysts: (a) Co(3)-Mn/TiO₂ and (b) Co/TiO₂.

The NO_x-TPD result of Co/TiO₂ shows an obvious peak at 345 °C which confirmed that TiO₂ supported single component (Mn or Co) catalyst is not beneficial for the chemisorption of NO_x species. The interaction between Mn and Co could greatly lower the activation energy of chemisorption.

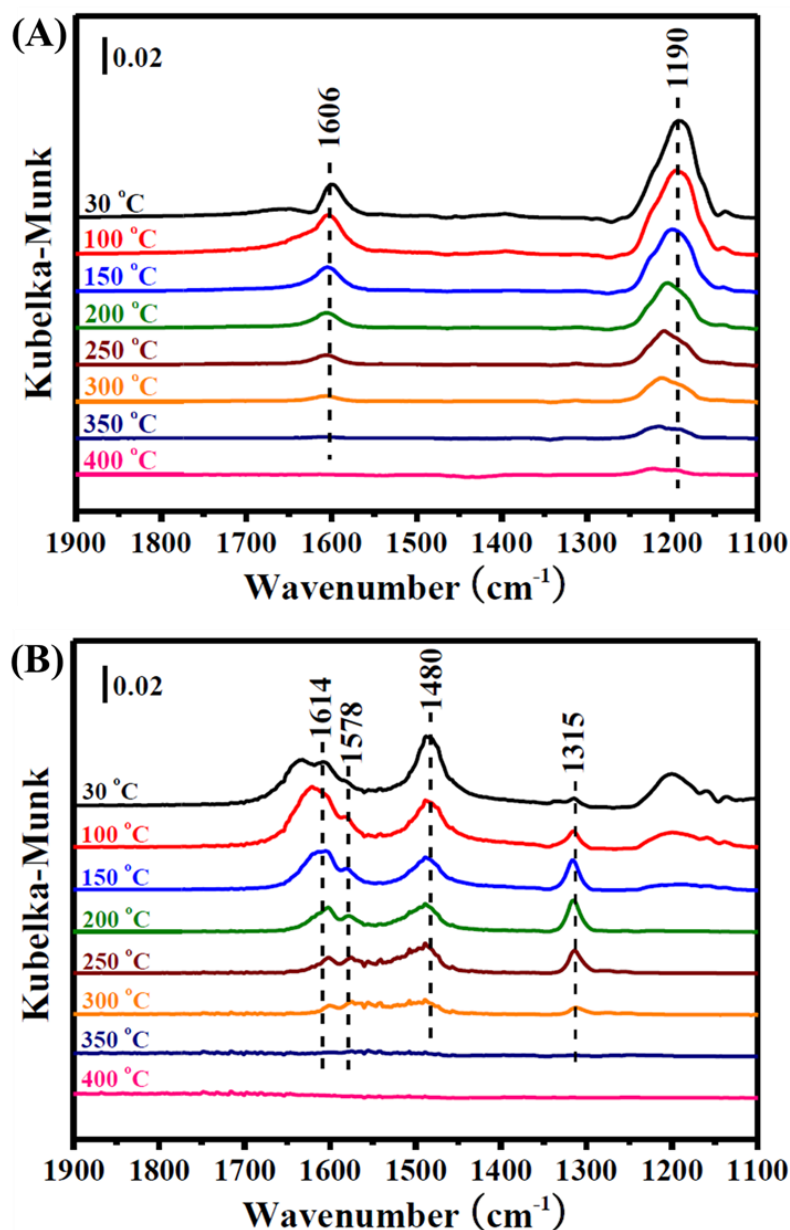


Figure S7. (A) *In situ* DRIFT spectra of NH₃ desorption on Co/TiO₂ as a function of temperature after the catalysts were exposed to a flow of 500 ppm NH₃ for 60 min. (B) *In situ* DRIFT spectra of NO_x desorption on Co/TiO₂ as a function of temperature after the catalysts were exposed to a flow of 500 ppm NO + 5% O₂ for 60 min.

The surface adsorption species of NH₃ and NO_x over Co/TiO₂ is similar to that over Mn/TiO₂ and Co-Mn/TiO₂ catalysts. The broad peaks centered at 1606 and 1190 cm⁻¹ in Figure S7A can be assigned to the asymmetric and symmetric bending vibrations of NH₃ coordinated with Lewis acid sites. The bands at 1614, 1578, 1480 and 1315 cm⁻¹ in Figure S7B can be assigned to the asymmetric stretching vibration of gaseous NO₂, one of the split ν_3 vibrations of bidentate nitrates, the ν_3 stretch vibration of linear nitrites and the ν_3 stretch vibration of monodentate nitrites, respectively.

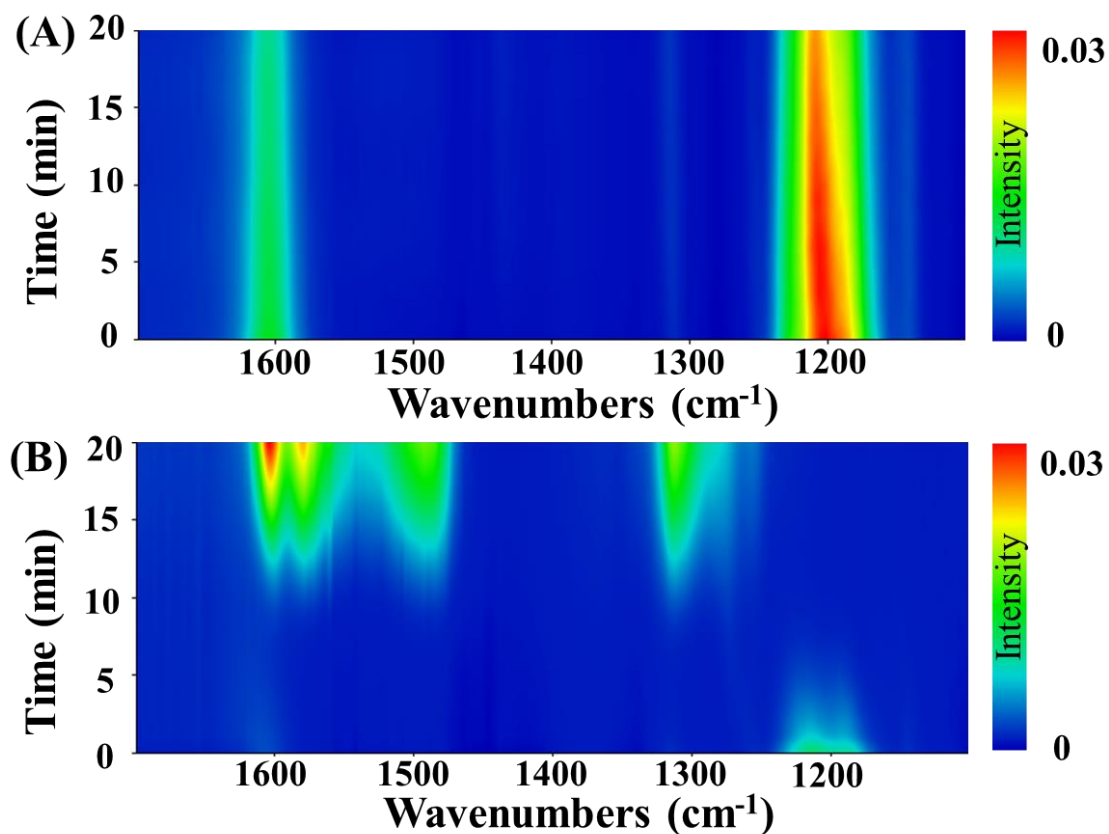


Figure S8. *In situ* DRIFT spectra of the transient reactions at (A) 150 °C and (B) 270 °C between NO+O₂ and preadsorbed NH₃ species over the Co/TiO₂ catalyst recorded as a function of time.

According to the results, the adsorbed NH₃ species can be hardly consumed by a continuous introduction of NO+O₂ at 150 °C, which is consistent with the catalytic performance. While at 270 °C, the NH₃ species showed an obvious decrease which consists of a considerable amount of desorption.

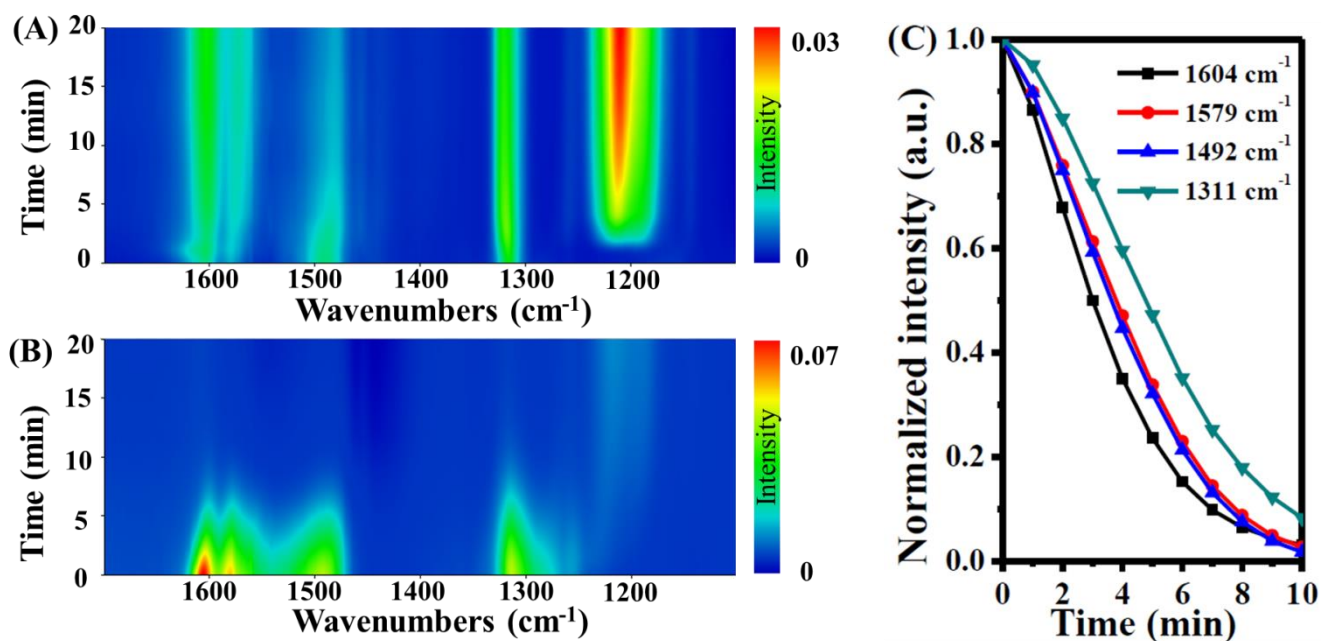


Figure S9. *In situ* DRIFT spectra of the transient reactions at (A) 150 °C and (B) 270 °C between NH₃ and preadsorbed NO+O₂ species over the Co/TiO₂ catalyst recorded as a function of time. (C) Consumption of different NO_x species at 270 °C upon passing NH₃ over NO+O₂-preadsorbed Co/TiO₂ catalyst.

The adsorption of NO+O₂ also leads to the formation of four NO_x species: gaseous NO₂ (1604 cm⁻¹), bidentate nitrates (1579 cm⁻¹), linear nitrites (1498 cm⁻¹) and monodentate nitrites (1311 cm⁻¹). The NO_x species remain stable on the catalyst surface at 150 °C which indicates no reaction occurred. When the transient reaction took place at 270 °C, the NO_x species showed an obvious decrease in which the desorption cannot be overlooked.

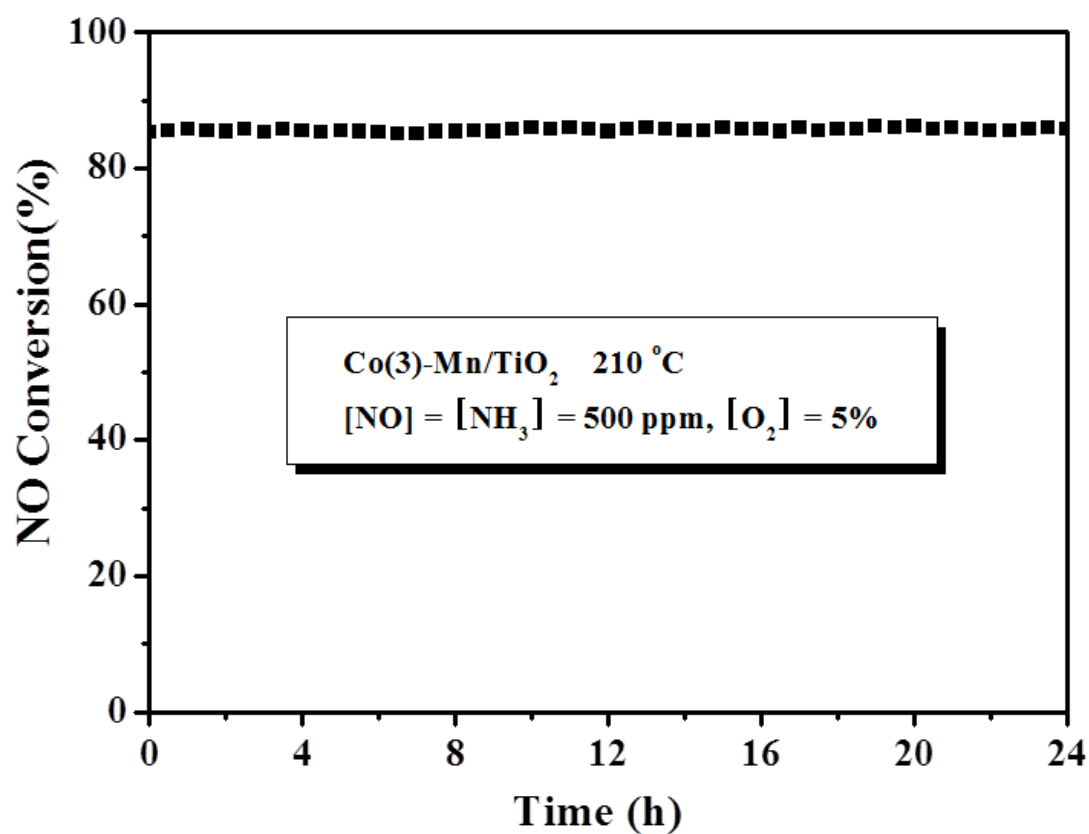


Figure S10. Stability test of the Co(3)-Mn/TiO₂ catalyst at 210 °C. Reaction conditions: 500 ppm NO, 500 ppm NH₃, 5 vol% O₂, N₂ as balance gas, total flow rate 270 mL/min and GHSV= 40 000 h⁻¹.

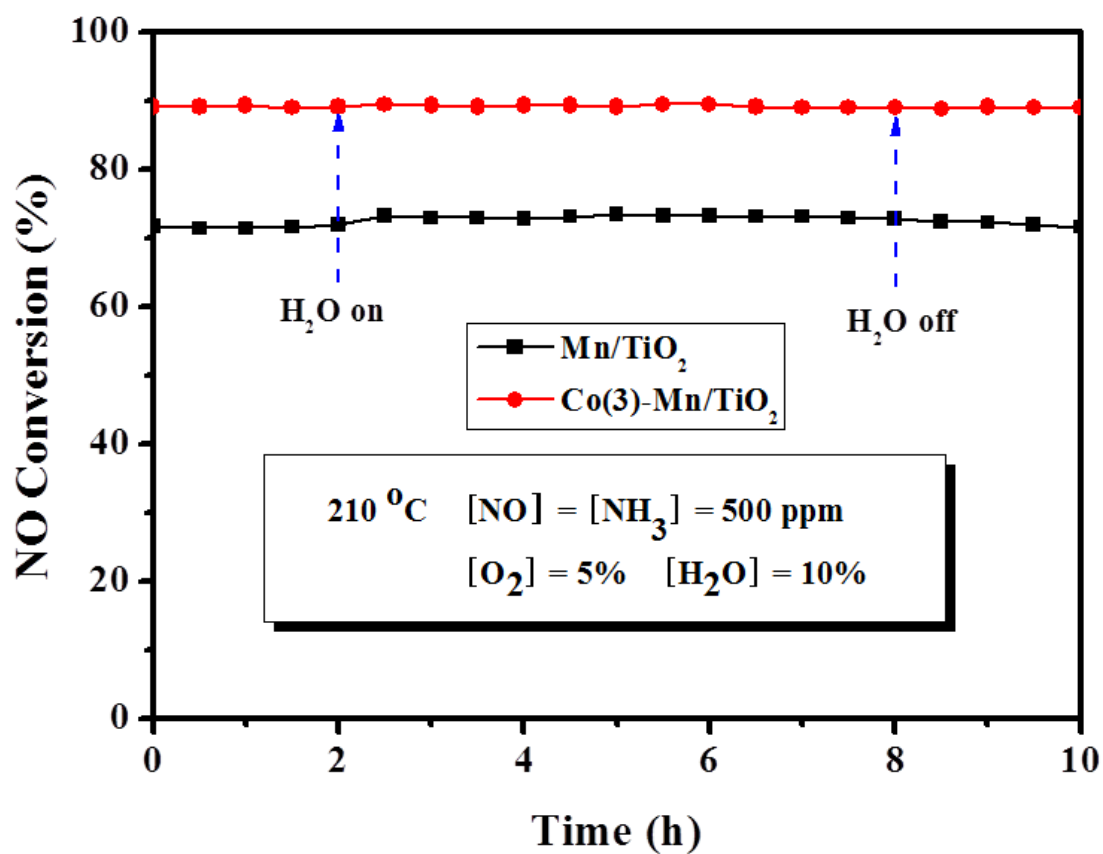


Figure S11. H₂O tolerance tests of the catalysts at 210 °C. Reaction conditions: 500 ppm NO, 500 ppm NH₃, 5 vol% O₂, 10 vol% H₂O (when used), N₂ as balance gas, total flow rate 270 mL/min and GHSV= 40 000 h⁻¹.

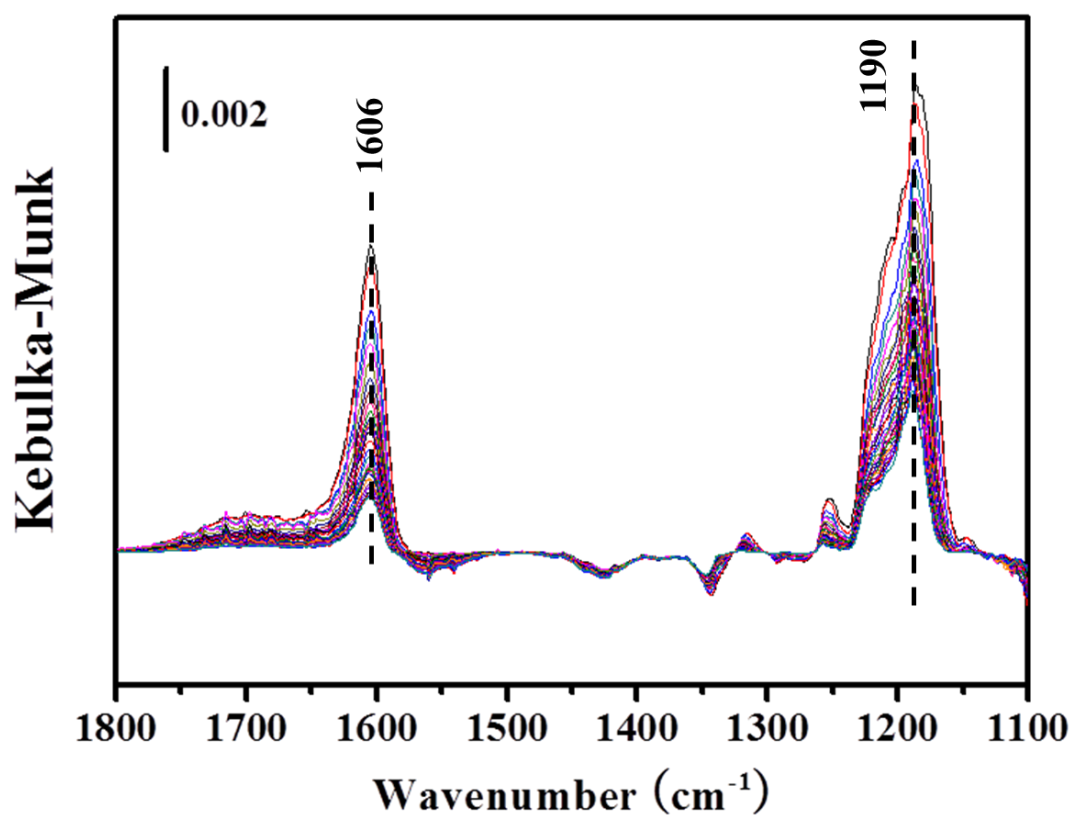


Figure S12. *In situ* DRIFT spectra of NH₃ desorption on the Mn/TiO₂ catalyst at 270 °C as a function of time at 1 min interval (30 min) after the catalysts were exposed to a flow of 500 ppm NH₃ for 60 min.

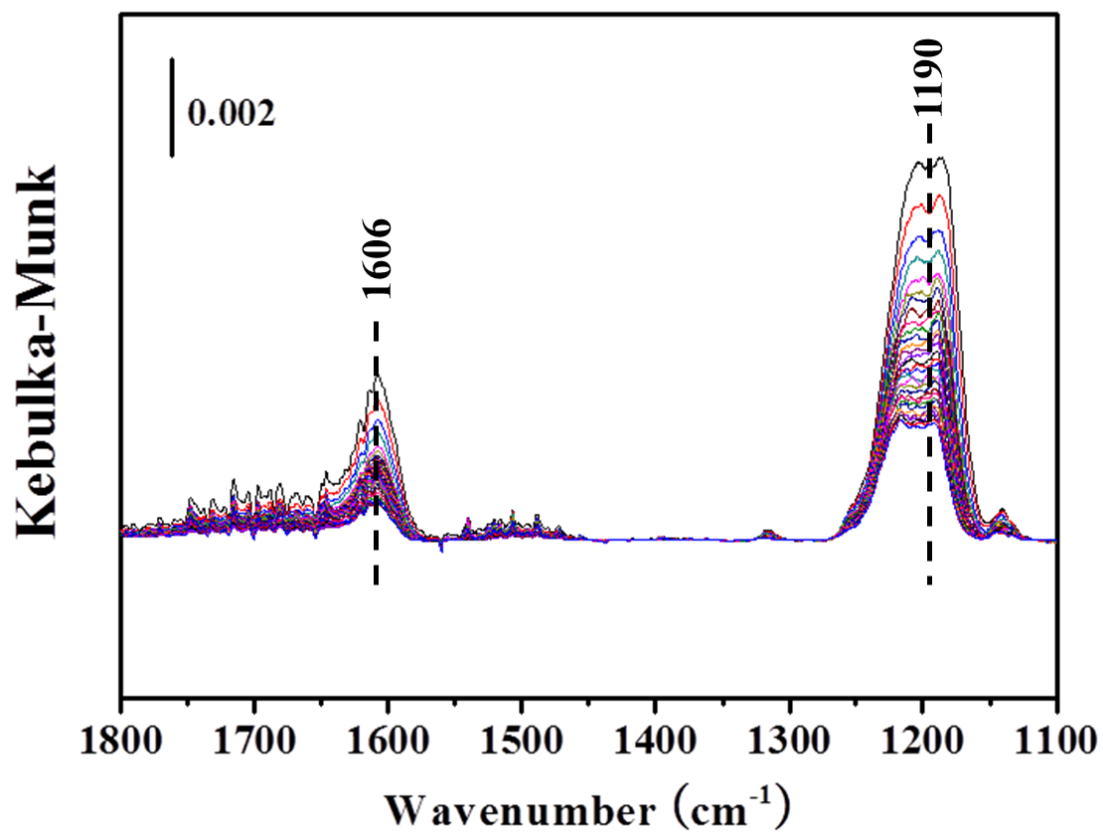


Figure S13. *In situ* DRIFT spectra of NH₃ desorption on the Co(3)-Mn/TiO₂ catalyst at 270 °C as a function of time at 1 min interval (30 min) after the catalysts were exposed to a flow of 500 ppm NH₃ for 60 min.

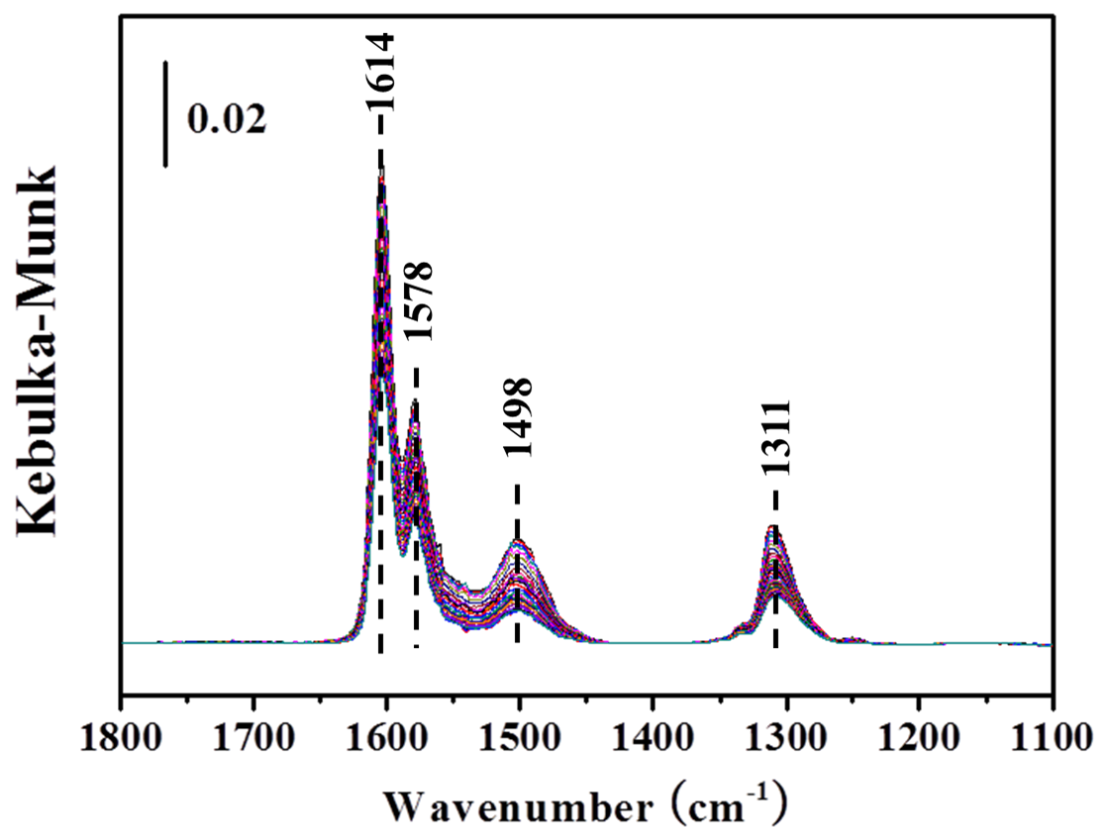


Figure S14. *In situ* DRIFT spectra of NO_x desorption on the Mn/TiO₂ catalyst at 270 °C as a function of time at 1 min interval (30 min) after the catalysts were exposed to a flow of 500 ppm NO + 5% O₂ for 60 min.

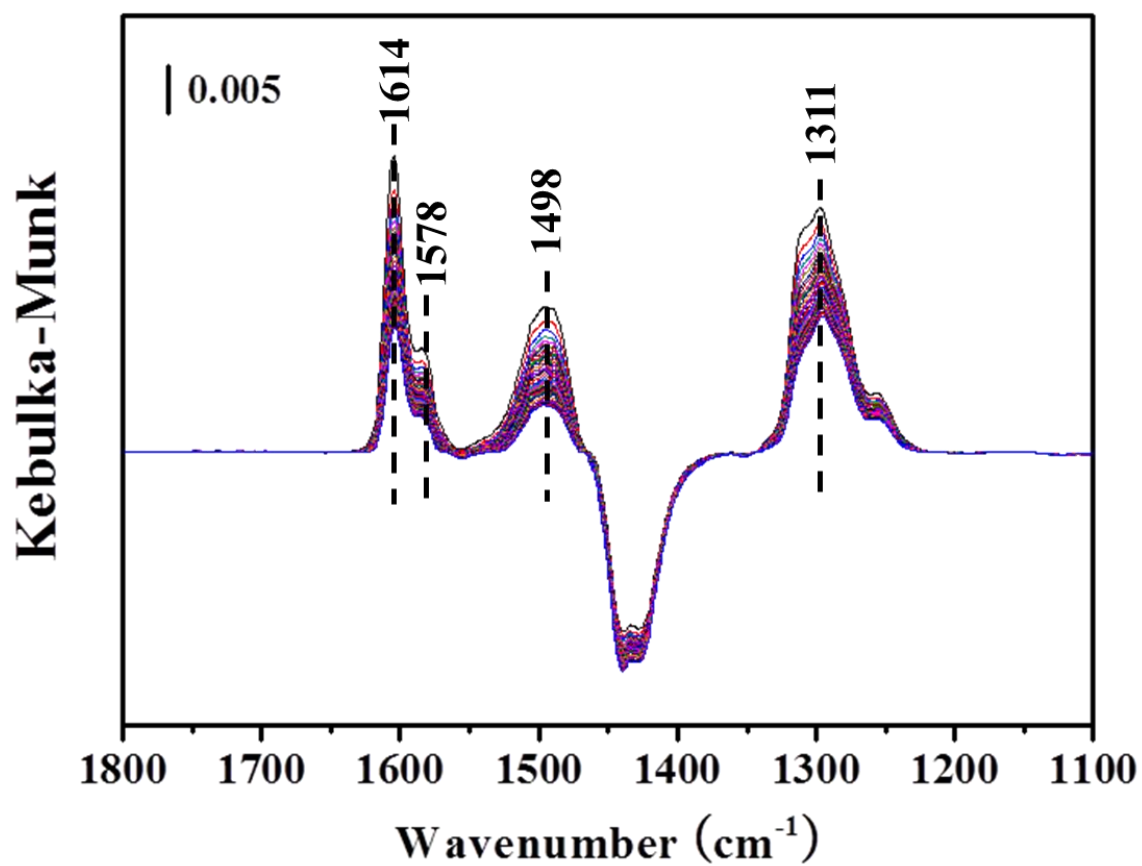


Figure S15. *In situ* DRIFT spectra of NO_x desorption on the Co(3)-Mn/TiO_2 catalyst at 270 $^{\circ}\text{C}$ as a function of time at 1 min interval (30 min) after the catalysts were exposed to a flow of 500 ppm NO + 5% O_2 for 60 min.

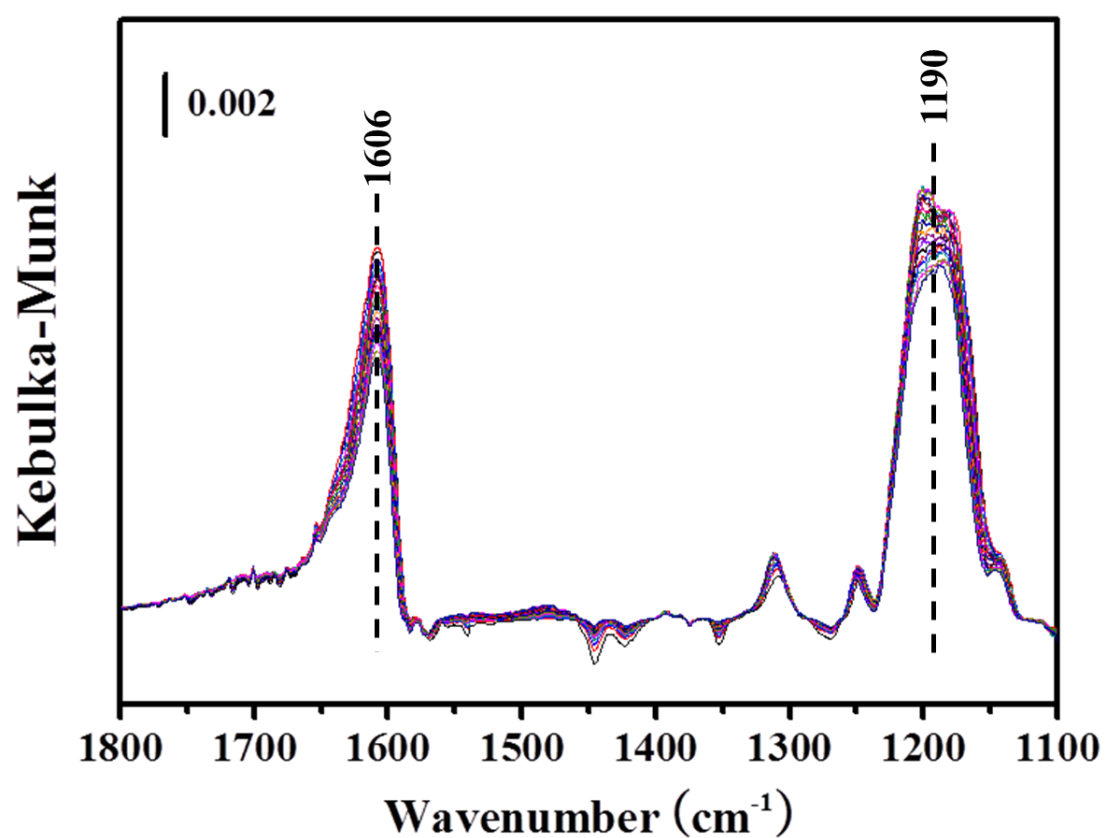


Figure S16. DRIFT spectra of transient reaction at 150 °C between NO+O₂ and preadsorbed NH₃ species over the Mn/TiO₂ catalyst recorded as a function of time (20 min).

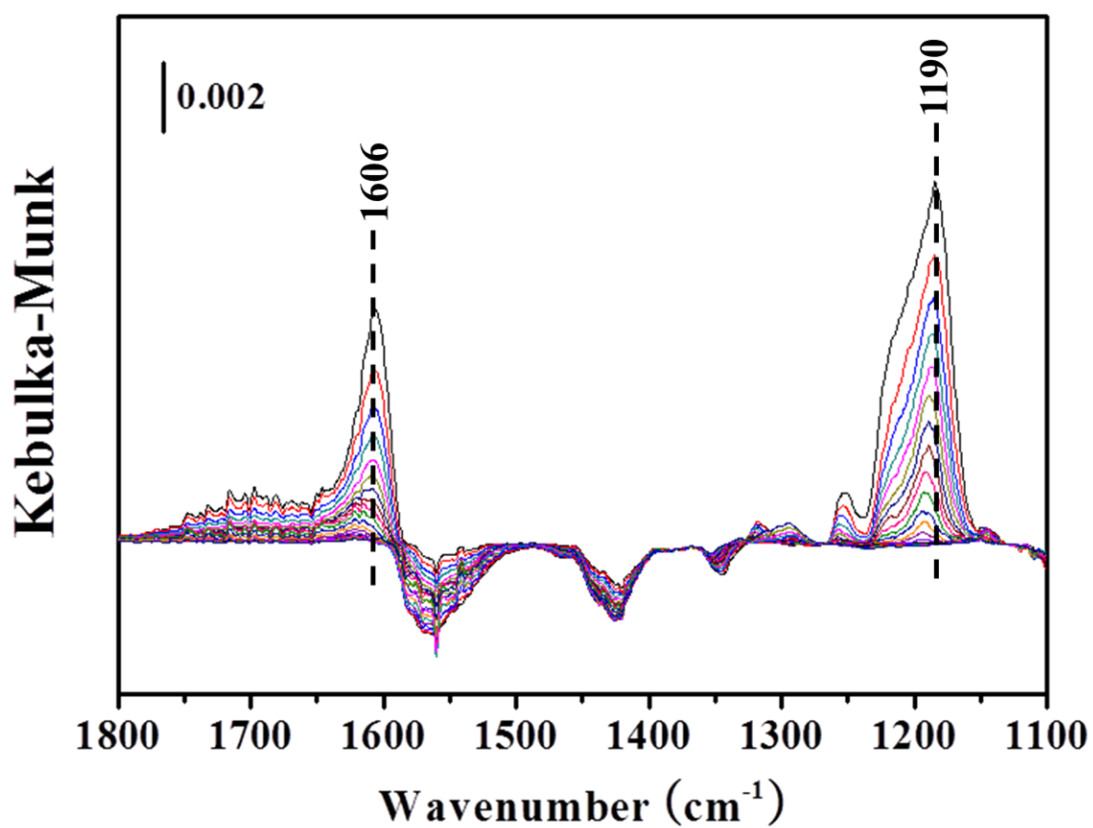


Figure S17. DRIFT spectra of transient reaction at 270 °C between NO+O₂ and preadsorbed NH₃ species over the Mn/TiO₂ catalyst recorded as a function of time (20 min).

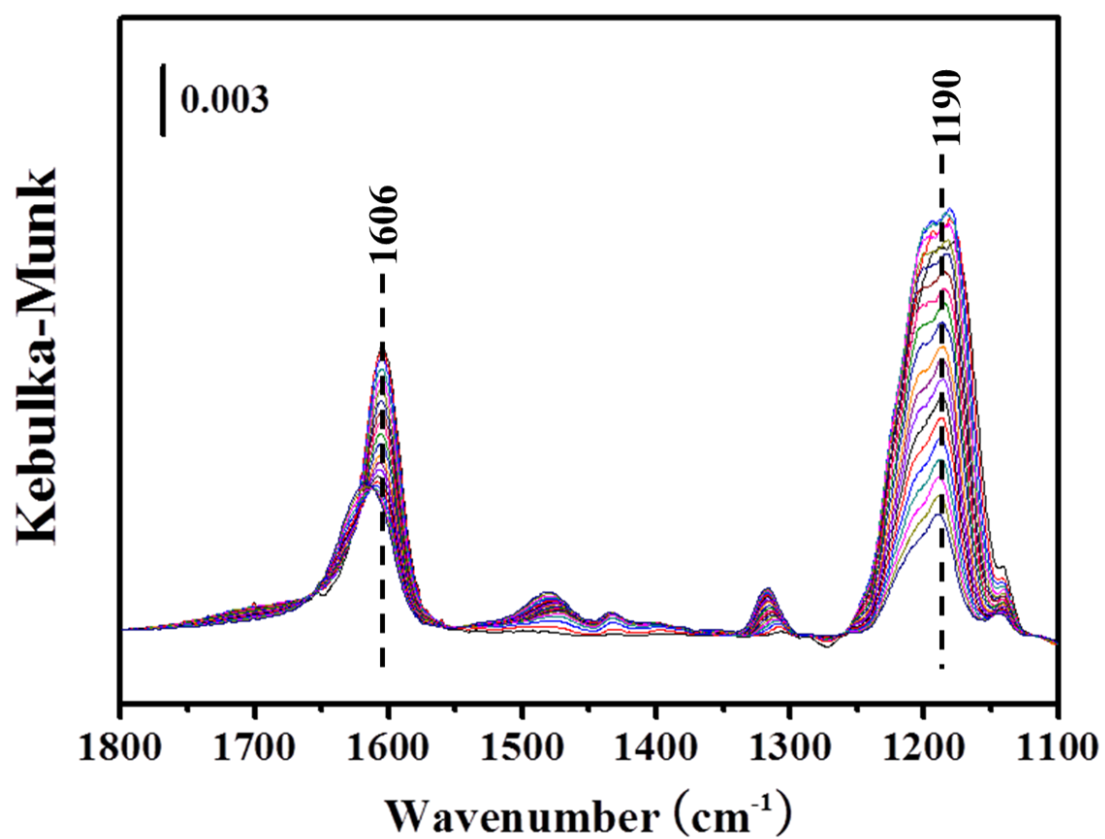


Figure S18. DRIFT spectra of transient reaction at 150 °C between NO+O₂ and preadsorbed NH₃ species over the Co(3)-Mn/TiO₂ catalyst recorded as a function of time (20 min).

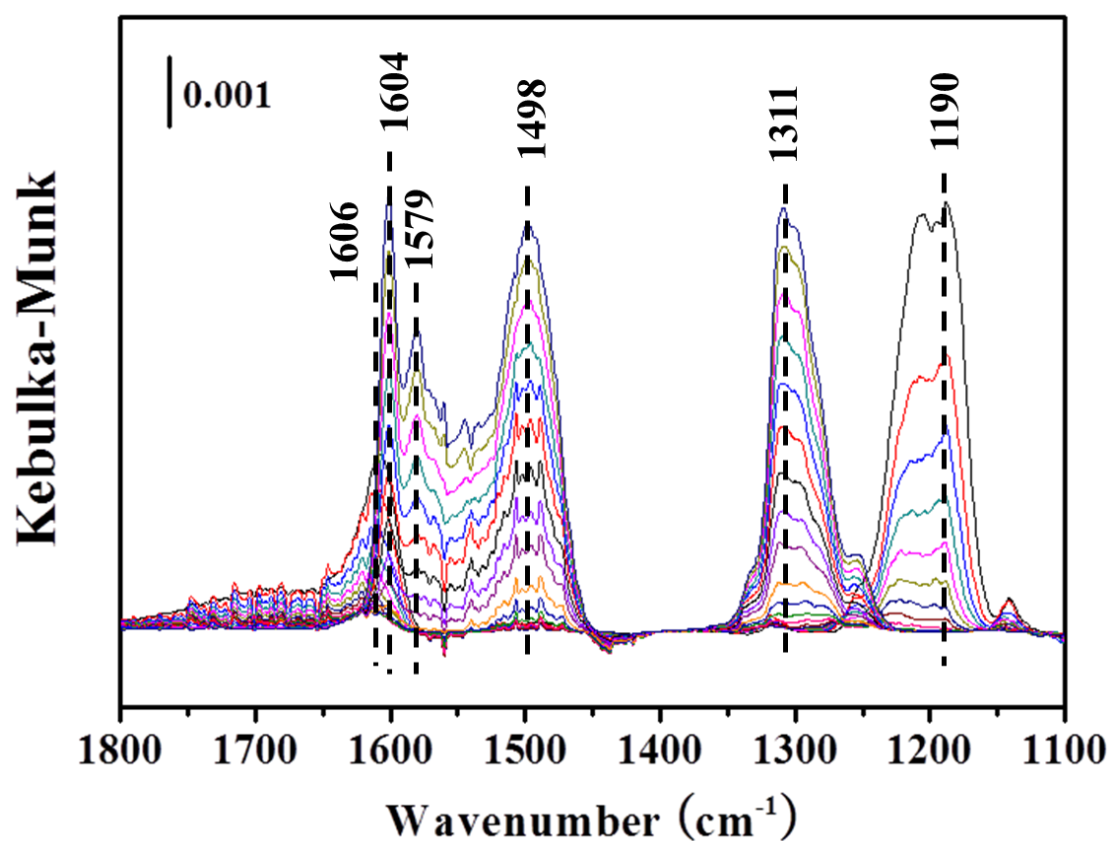


Figure S19. DRIFT spectra of transient reaction at 270 °C between $\text{NO} + \text{O}_2$ and preadsorbed NH_3 species over the Co(3)-Mn/TiO_2 catalyst recorded as a function of time (20 min).

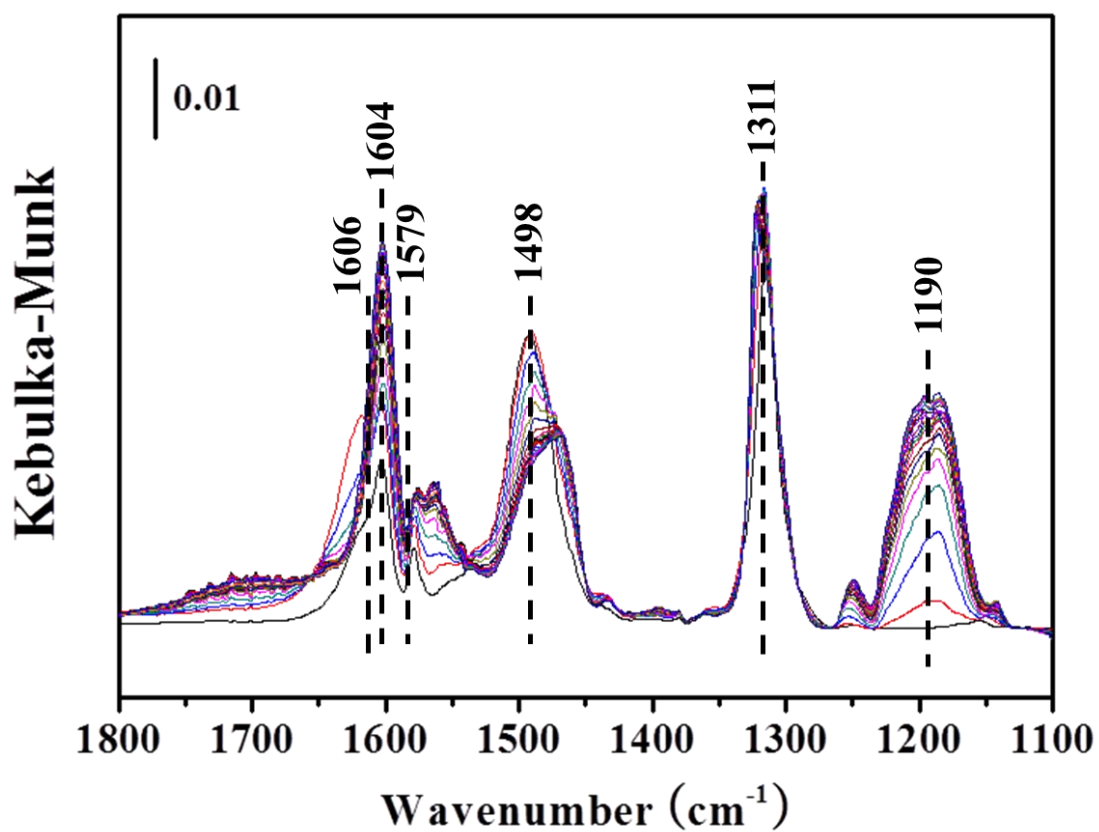


Figure S20. DRIFT spectra of transient reaction at 150 °C between NH₃ and preadsorbed NO+O₂ species over the Mn/TiO₂ catalyst recorded as a function of time (20 min).

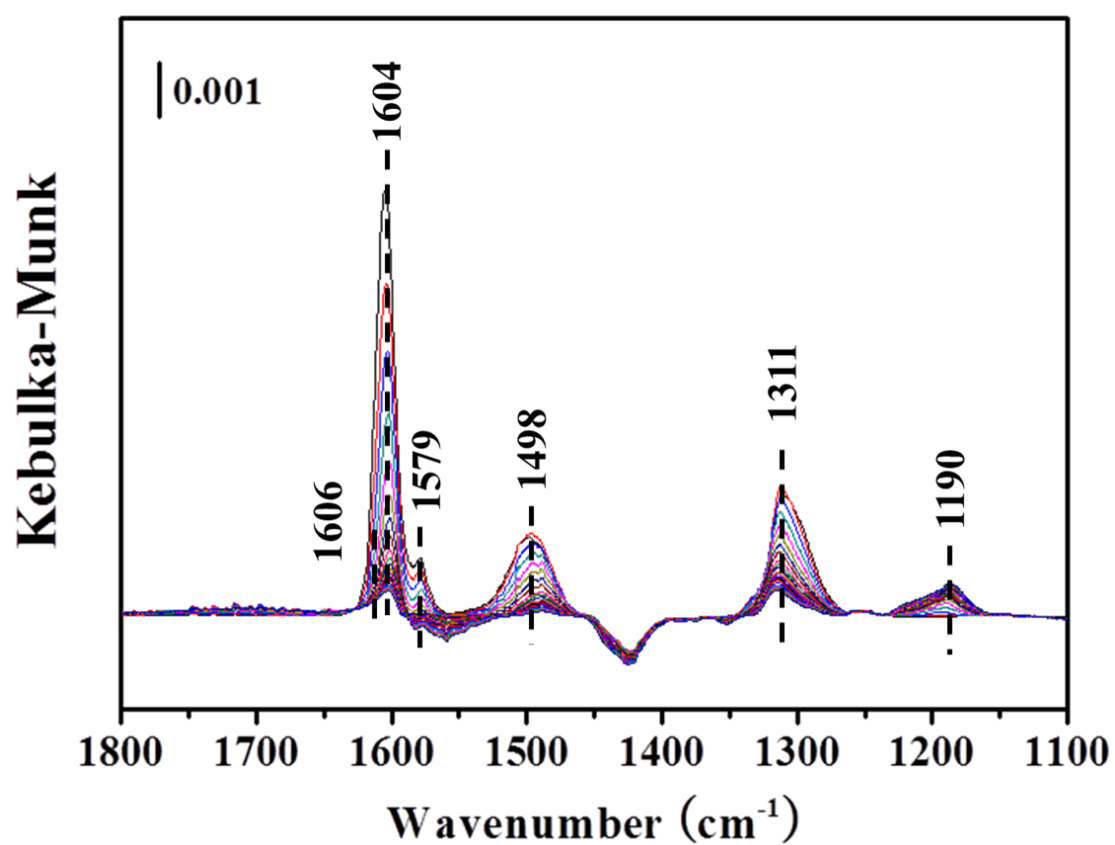


Figure S21. DRIFT spectra of transient reaction at 270 °C between NH₃ and preadsorbed NO+O₂ species over the Mn/TiO₂ catalyst recorded as a function of time (20 min).

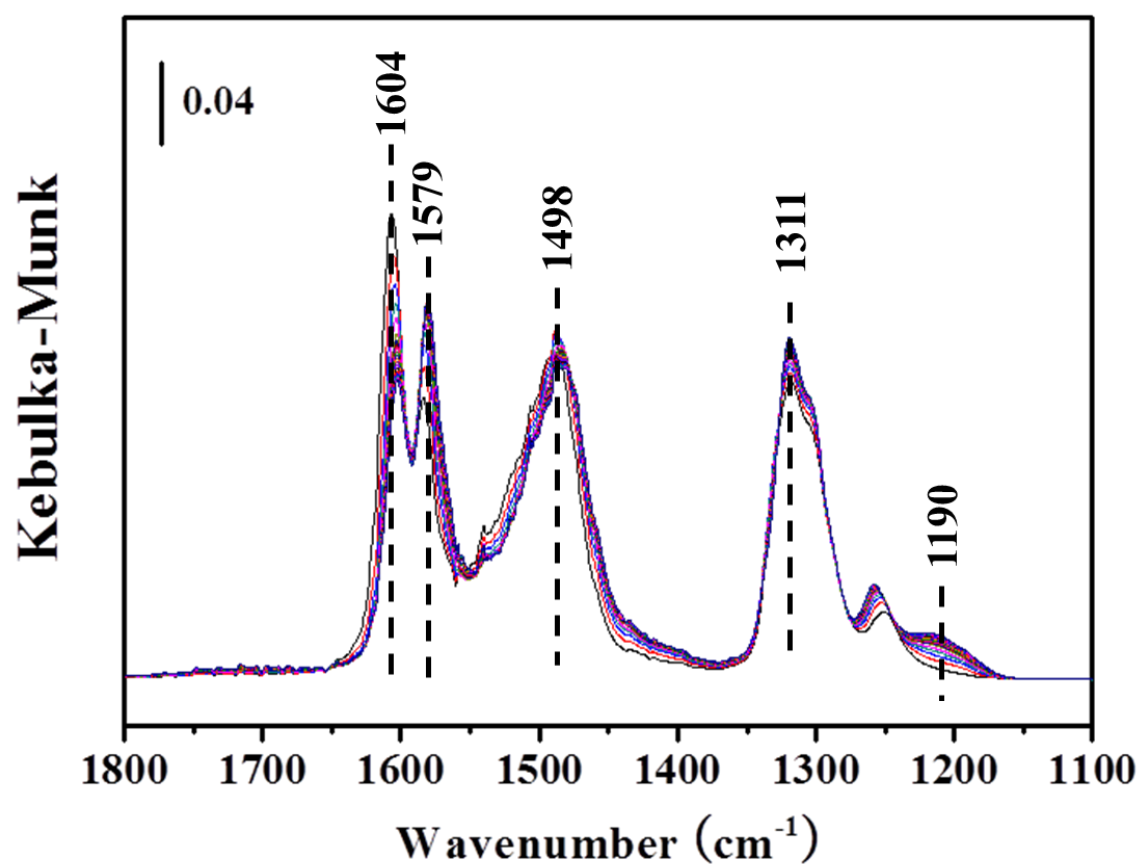


Figure S22. DRIFT spectra of transient reaction at 150 °C between NH₃ and preadsorbed NO+O₂ species over the Co(3)-Mn/TiO₂ catalyst recorded as a function of time (20 min).

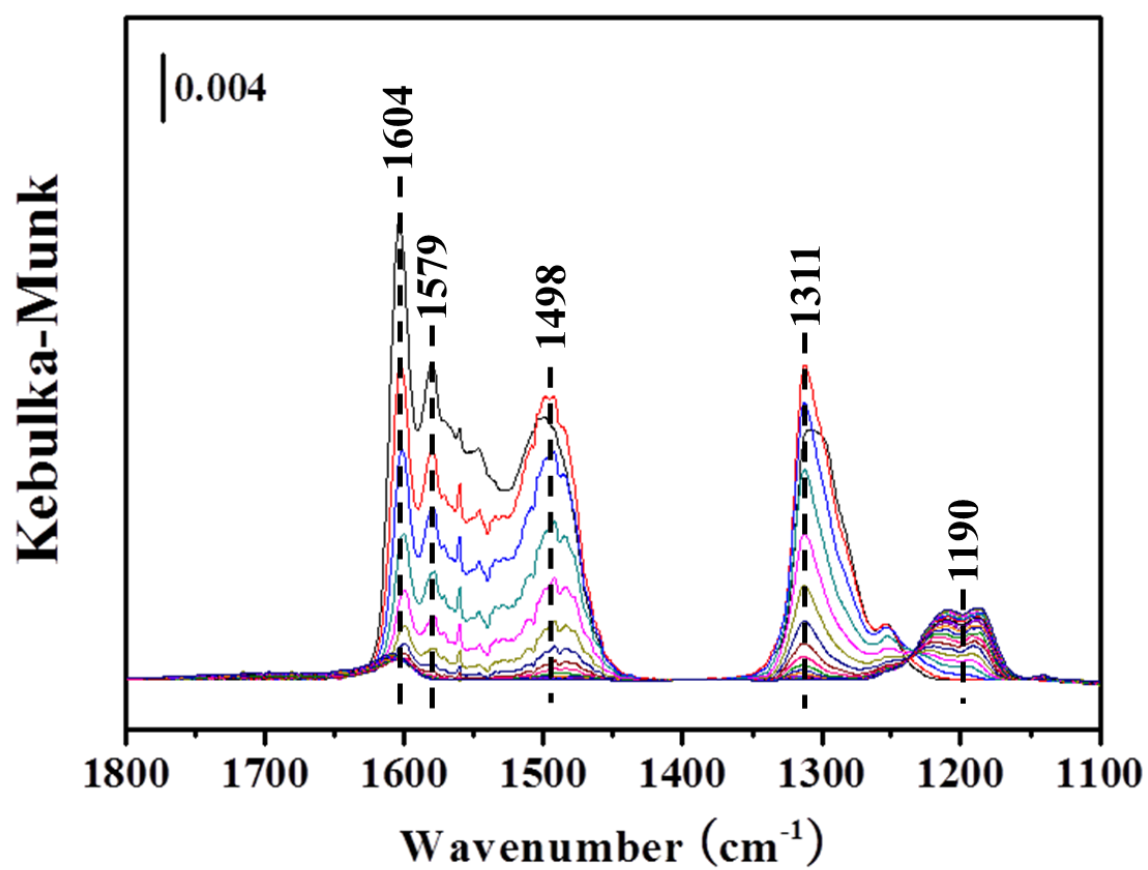


Figure S23. DRIFT spectra of transient reaction at 270 °C between NH₃ and preadsorbed NO+O₂ species over the Co(3)-Mn/TiO₂ catalyst recorded as a function of time (20 min).

Table S2. Total Amount of Adsorbed NH₃ on the Catalysts

catalyst	Acidity ^a (μmol/g)
Mn/TiO ₂	8.36
Co(1)-Mn/TiO ₂	6.68
Co(2)-Mn/TiO ₂	6.37
Co(3)-Mn/TiO ₂	8.04
Co(4)-Mn/TiO ₂	6.77
Co(6)-Mn/TiO ₂	5.26
Co(8)-Mn/TiO ₂	4.85
Co/TiO ₂	5.47

^aCalculated from the NH₃-TPD results.