

Supplementary Material

Modification of CrCeO_x with Mo: Improved SO₂ resistance and N₂ selectivity for NH₃-SCR at medium-low temperature

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This part of the data were the previous research data of our group, and the results are being published. In Fig A1, the NH₃ adsorption peaks on CrCeO_x were mainly in the 900 ~ 1700 cm⁻¹ and 3100 ~ 3700 cm⁻¹ regions. The bands at 1012, 1237, and 1604 cm⁻¹ could be attributed to coordinated NH₃ on Lewis acid site.¹ Similarly, the bands at 987 as well as 1087 cm⁻¹ could be attributed to NH₃(ad) at Lewis acid site. The band at 1056 cm⁻¹ was attributed to an intermediate species (-NH₂) formed by the dehydrogenation reaction of NH₃, and the band at 1367 cm⁻¹ was attributed to the species formed by adsorption of ammonia oxidation.² The band at 1323 cm⁻¹ was attributed to NH₄⁺ species formed by adsorption NH₃ on the Brønsted acid sites.³ Three bands were observed in the N-H oscillation region at 3250, 3360 and 3160 cm⁻¹, respectively. The band at 3700 cm⁻¹ might belonged to the O-H oscillatory bond on the surface.⁴ It indicated that the Lewis acid site is dominant on the catalyst surface and exist mainly in coordinated NH₃(ad). The intensity of the bands attributed to coordinated NH₃ at 987, 1012, 1232 and 1604 cm⁻¹ decreased rapidly after the introduction of NO + O₂. The band at 1580 cm⁻¹ could be attributed to the bidentate nitrate species formed after NO adsorption.^{5,6} While the new band at 1280 cm⁻¹ was attributed to the area of overlap between NH₃(ad) and NO adsorbed, therefore cannot be classified. During the first few minutes, the band at 1323 cm⁻¹ was attributed to NH₄⁺ ions did not change. With the continuous flux of NO and O₂, the band intensity at NH₄⁺ began to gradually decrease. After 5 min, the bands of nitrate species generated after the introduction of NO + O₂ also started to

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appear and weakened with the increasing time. The overlapping bands at 1280 cm^{-1} also gradually weakened, indicating that NH_4^+ was consumed. It could be concluded that the bands attributed to the pre-adsorbed NH_3 started to weaken and the adsorbed $\text{NH}_3(\text{ad})$ species on Lewis acid site disappeared rapidly with the introduction of $\text{NO} + \text{O}_2$, indicating that the reaction proceeded rapidly. The band at 1353 cm^{-1} might be NH_4^+ migrating to the higher band or it may be an intermediate product generated by the reaction between adsorbed NH_3 and NO_x .^{1,7} In this paper, the band attributed to NH_4^+ adsorbed on the Brønsted acid also weakened significantly with time, so the band at 1353 cm^{-1} was attributed to the intermediate species, indicated that NH_4^+ ions on Brønsted acid site also participated in SCR process. The band at 1085 cm^{-1} did not change with time. It has been reported that there is a band at 1045 cm^{-1} could be assigned to $\text{Cr}=\text{O}$.⁸ In contrast, the XPS results indicated that Cr was mainly in 3^+ as well as 6^+ and did not contain Cr^{2+} . Therefore, the band at 1045 cm^{-1} was assigned to Cr(III)=O .

As shown in Fig A2, the intensity of the adsorption peak by $\text{NO} + \text{O}_2$ was much weaker than that of NH_3 , which most likely due to the lack of basic sites on the catalyst surface. The bands at 1263 and 1376 cm^{-1} were attributed to bridged nitrate species.⁴ When introduction of NH_3 , new oscillation bands were observed at 1250 , 1307 , and 1604 cm^{-1} . The band at 1604 cm^{-1} was attributed to $\text{NH}_3(\text{ad})$. Since the intensity of the adsorption peak of NO_x was much lower than that of $\text{NH}_3(\text{ad})$, the band at 1250 cm^{-1} was attributed to $\text{NH}_3(\text{ad})$. The band at 1307 cm^{-1} was attributed to the migration of NH_4^+ from 1323 cm^{-1} .⁹ With the increase of adsorption time, the adsorption peak of NO_x did not change significantly, indicated that the SCR process between $\text{NH}_3(\text{g})$ and $\text{NO}_x(\text{ad})$ did not react.

From the results of *in-situ* DRIFTS, it could be observed that NH_3 is strongly adsorbed on the surface of CrCeO_x , generating $\text{NH}_3(\text{ad})$ and NH_4^+ , of which $\text{NH}_3(\text{ad})$ was dominant. The adsorption strength of NO_x on the surface was weaker than that of NH_3 . The NH_3 -SCR process could occur between adsorbed $\text{NH}_3(\text{ad})$ and $\text{NO}(\text{g})$, but not between co-adsorbed $\text{NO}_x(\text{ad})$ and NH_3 , indicated to the E-R mechanism.

Notes and references

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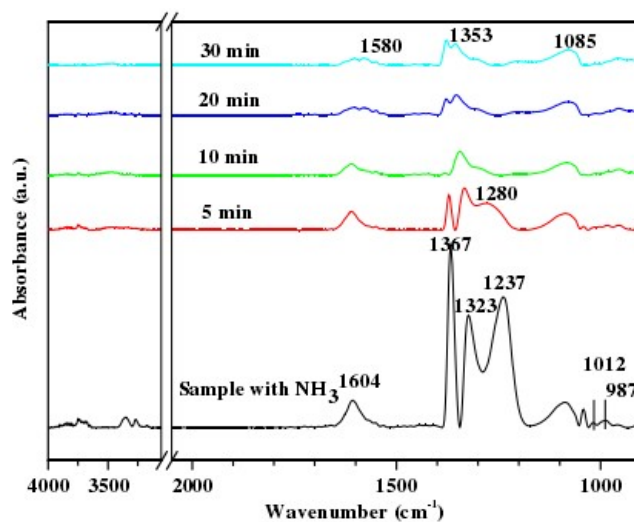


Fig. A1 DRIFT spectra of CrCeO_x pretreated by 1000 ppm NH₃ followed by exposed to 1000 ppm NO + 3% O₂ for various times.

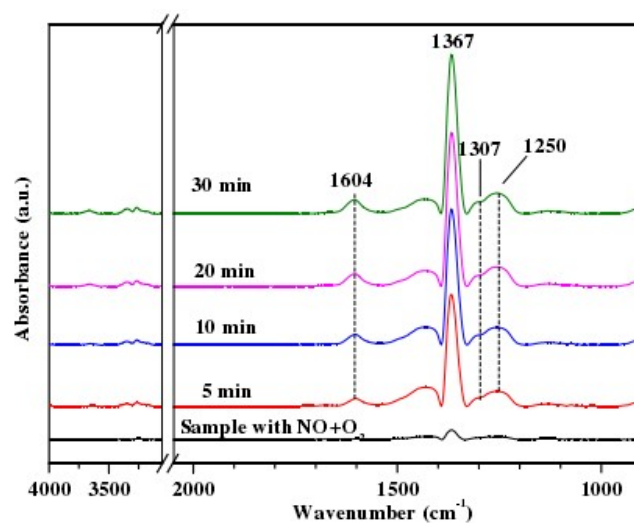


Fig. A2 DRIFT spectra of CrCeO_x pretreated by 1000 ppm NO + 3% O₂ followed by exposed to 1000 ppm NH₃ for various times.

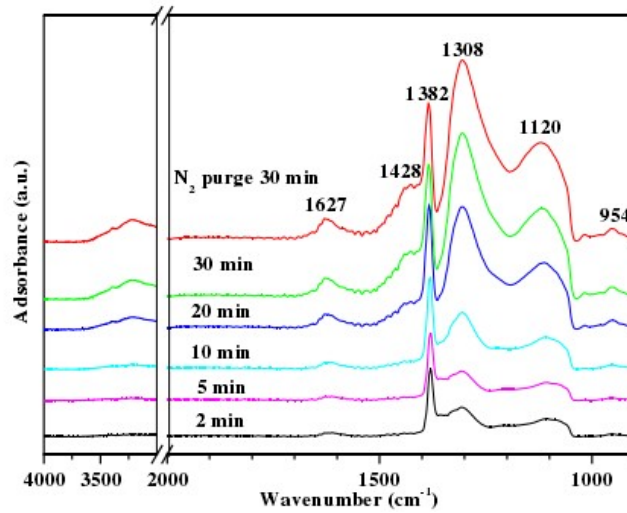


Fig. A3 DRIFT spectra of CrCeO_x exposed to SO₂ + O₂ for various times and purged by N₂ for 30 min.

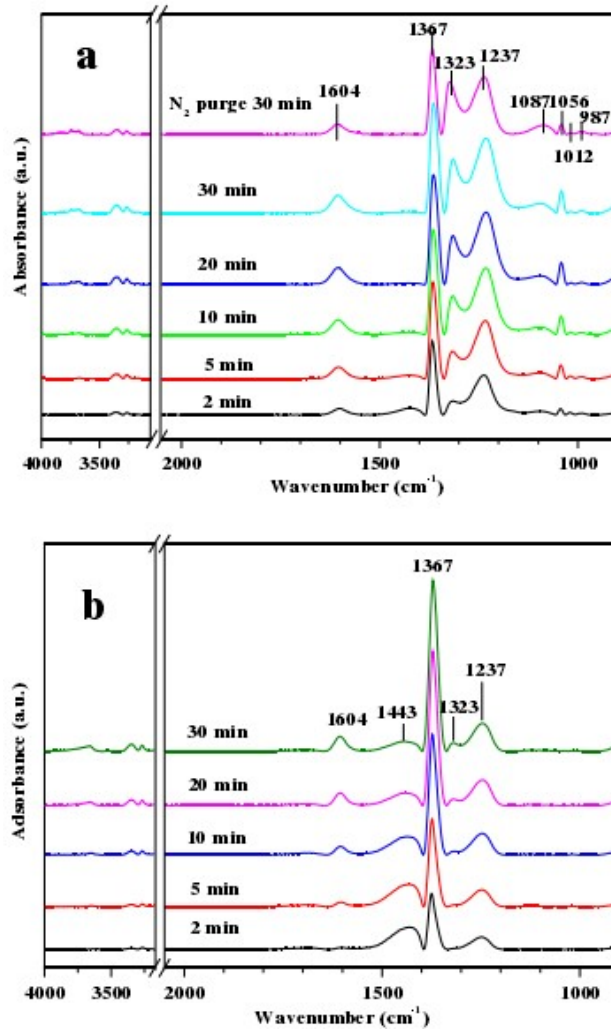


Fig. A4 DRIFT spectra of NH₃ adsorption on fresh and sulfated CrCeO_x for various times.

a: Fresh Cr-CeO_x, b: sulfated Cr-CeO_x

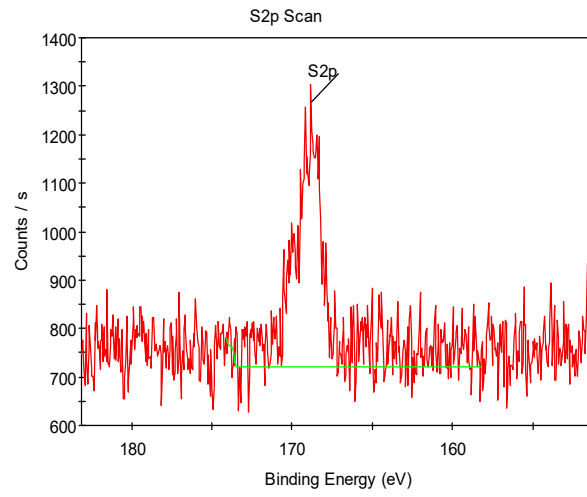


Fig. A5 The S2p scan spectrum of CrCeO_x-s.

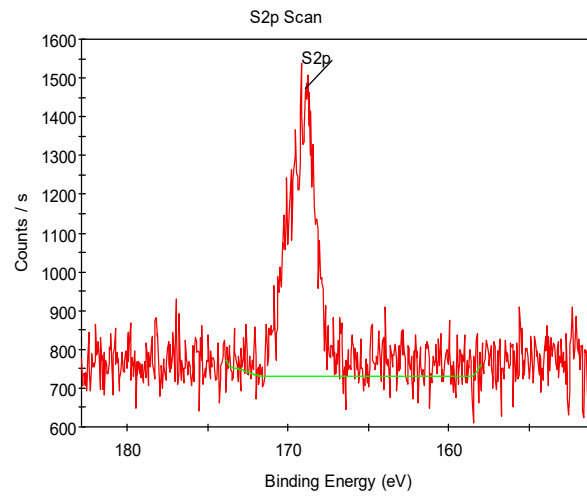


Fig. A6 The S2p scan spectrum of Mo(0.3)-CrCeO_x-s.