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Supporting information

The promoting effect of support pretreatment with sulfate acid on Ca resistance of CeO_2/ZrO_2 catalyst for NH_3-SCR of NO_x with NH_3

Chenglong Li[a], Zhitao Han[a]*, Xinxin Wang[a], Yu Gao[a], Zhen Wang[a], Xinxiang Pan[a b]

a. Marine Engineering College, Dalian Maritime University, Dalian 116026, China;

b. School of Electronic and Information Technology, Guangdong Ocean University, Zhanjiang 524088, China

Correspondence information: Dr. Zhitao Han, Dalian Maritime University, No.1, Linghai Road, Dalian 116026, China, hanzt@dlmu.edu.cn

Table. S1 Summary of literature data on NH_3-SCR catalysts over alkali metal poisoned

Catalysts	Preparation method	Reaction condition	Fresh catalysts $T_{80\%}$, ºC	Alkali metals precursor and load	Poisoned catalysts		Ref
					$T_{80\%}$, ºC	Max NO_x Con, %	
CeO_2/ZrO_2-S	Precipitation (ZrO_2) Impregnation	[NO] = [NH_3] = 500 ppm, [O_2] = 5 vol. %, N_2 as balance GHSV = 60,000 h^{-1}	245-500	($Ca(NO_3)_2$) 1 wt.% CaO ($Ca(NO_3)_2$) 2 wt.% CaO ($Ca(NO_3)_2$) 5 wt.% CaO	255-490 280-480 -	100 100 30	This work
CeO_2/SO_4^{2-}-ZrO_2	Impregnation	[NO] = [NH_3] = 500 ppm, [O_2] = 3.5 vol. %, N_2 as balance GHSV = 180,000 h^{-1}	360-545	(KNO_3) K/Ce = 0.4 (KNO_3) K/Ce = 0.8 K/Ce was molar ratio	325-530 375-475 -	100 86 -	1
V-$Ce(SO_4)_2$/Ti	Impregnation	[NO] = [NH_3] = 500 ppm, [O_2] = 3.5 vol. %, N_2 as balance GHSV = 150,000 h^{-1}	275-450	($NaHCO_3$) 0.5 wt.% Na	-	80	2
V_2O_5-WO_3/TiO_2	Impregnation	[NO] = [NH_3] = 500 ppm, [O_2] = 3 vol. %, N_2 as balance GHSV = 240,000 h^{-1}	280-500	(CaO) 2 wt.% CaO ($CaCO_3$) 2 wt.% CaO ($CaSO_4$) 2 wt.% CaO	- - 325-480	63 55 90	3
V_2O_5-WO_3/TiO_2	Impregnation	[NO] = [NH_3] = 500 ppm, [O_2] = 3 vol. %, N_2 as balance GHSV = 70,000 h^{-1}	240-500	($Ca(HO)_2$) 0.1 wt.% CaO ($Ca(HO)_2$) 0.5 wt.% CaO ($Ca(HO)_2$) 1 wt.% CaO ($Ca(HO)_2$) 2 wt.% CaO	265-500 280-500 290-500 -	100 100 100 56	4

V_2O_5-WO_3/TiO_2	Impregnation	[NO] = [NH_3] = 500 ppm, [O_2] = 5 vol. %, N_2 as balance GHSV = 100,000 h^{-1}	225-400	($Ca(NO_3)_2$) The molar ratio of Ca/V was 1:1	-	73	5
V_2O_5-WO_3-CeO_2/ TiO_2	Impregnation	[NO] = [NH_3] = 500 ppm, [O_2] = 5 vol. %, N_2 as balance GHSV = 100,000 h^{-1}	180-400	($Ca(NO_3)_2$) The molar ratio of Ca/V was 1:1	240-400	96	6
CeO_2-WO_3	Impregnation Urea as precipitant	[NO] = [NH_3] = 500 ppm, [O_2] = 3 vol. %, N_2 as balance GHSV = 120,000 h^{-1}	195-450	($Ca(HO)_2$) 1 wt.% CaO ($Ca(HO)_2$) 3 wt.% CaO ($Ca(HO)_2$) 5 wt.% CaO	220-450 245-450 290-400	100 95 85	7
Ce/TiO_2	Sol-gel	[NO] = [NH_3] = 600 ppm, [O_2] = 3 vol. %, Ar as balance GHSV = 108,000 h^{-1}	210-400	($Ca(NO_3)_2$) The molar ratio of Ca/Ce was 0.05:1	-	64	8
Ce/TiO_2	Impregnation	[NO] = [NH_3] = 600 ppm, [O_2] = 3.5 vol. %, N_2 as balance GHSV = 100,000 h^{-1}	-	($Ca(NO_3)_2$) The molar ratio of Ca/Ce was *x*:1(x=0.25, 0.5, 1 and 2)	-	40 16 10 18	9
CeO_2-Nb_2O_5-TiO_2	Sol-gel	[NO] = [NH_3] = 1000 ppm, [O_2] = 3 vol. %, N_2 as balance GHSV = 90,000 h^{-1}	230-490	(KNO_3) The molar ratio of K/Ce was 0.2:1	295-425	85	10
Ce/TNTs-eth	Impregnation	[NO] = [NH_3] = 600 ppm, [O_2] = 3.5 vol. %, N_2 as balance GHSV = 100,000 h^{-1}	270-500	(KNO_3) K/Ce=0.25 ($Ca(NO_3)_2$) Ca/Ce=0.25 ($NaNO_3$) Na/Ce=0.25	330-440 310-470 295-470	88 96 98	11

Mn-Ce-Ti	Precipitation	[NO] = [NH_3] = 500 ppm, [O_2] = 3 vol. %, N_2 as balance GHSV = 18,000 h^{-1}	150-330	($Ca(HO)_2$) 2 wt.% Ca ($CaCl_2$) 2 wt.% Ca	- -	80 77	12
Mn/TiO_2	Impregnation	[NO] = [NH_3] = 1000 ppm, [O_2] = 3 vol. %, N_2 as balance GHSV = 75,000 h^{-1}	100-200	($Ca(NO_3)_2$) 0.5 wt.% Ca ($Ca(NO_3)_2$) 1 wt.% Ca ($Ca(NO_3)_2$) 3 wt.% Ca ($Ca(NO_3)_2$) 5 wt.% Ca ($Ca(NO_3)_2$) 10 wt.% Ca	125-200 147-200 136-200 147-200 130-200	100 100 100 97 100	13
Fe-Ce/TiO_2	Precipitation	[NO] = [NH_3] = 500 ppm, [O_2] = 3 vol. %, N_2 as balance GHSV = 18,000 h^{-1}	220-360	($Ca(HO)_2$) 1 wt.% Ca ($Ca(HO)_2$) 2 wt.% Ca ($Ca(HO)_2$) 3 wt.% Ca	- - -	76 74 64	14
Fe-Ce/TiO_2	Precipitation	[NO] = [NH_3] = 500 ppm, [O_2] = 3 vol. %, N_2 as balance GHSV = 18,000 h^{-1}	220-360	($CaCO_3$) 1 wt.% Ca ($CaCO_3$) 2 wt.% Ca ($CaCO_3$) 3 wt.% Ca	250-360 265-360 270-360	90 89 88	15
Zr-Cu/SZM-5	Impregnation	[NO] = [NH_3] = 500 ppm, [O_2] = 3 vol. %, N_2 as balance GHSV = 18,000 h^{-1}	160-400	($Ca(NO_3)_2$) 1.26 wt.% CaO	170-400	100	16
Cu-Ce/H-SPAO-34	Impregnation	[NO] = [NH_3] = 500 ppm, [O_2] = 3 vol. %, N_2 as balance GHSV = 30,000 h^{-1}	180-360	($Ca(NO_3)_2$) 1 wt.% Ca (KNO_3) 1 wt.% K ($Pb(NO_3)_2$) 1 wt.% Pb	210-360 210-360 200-360	100 100 100	17

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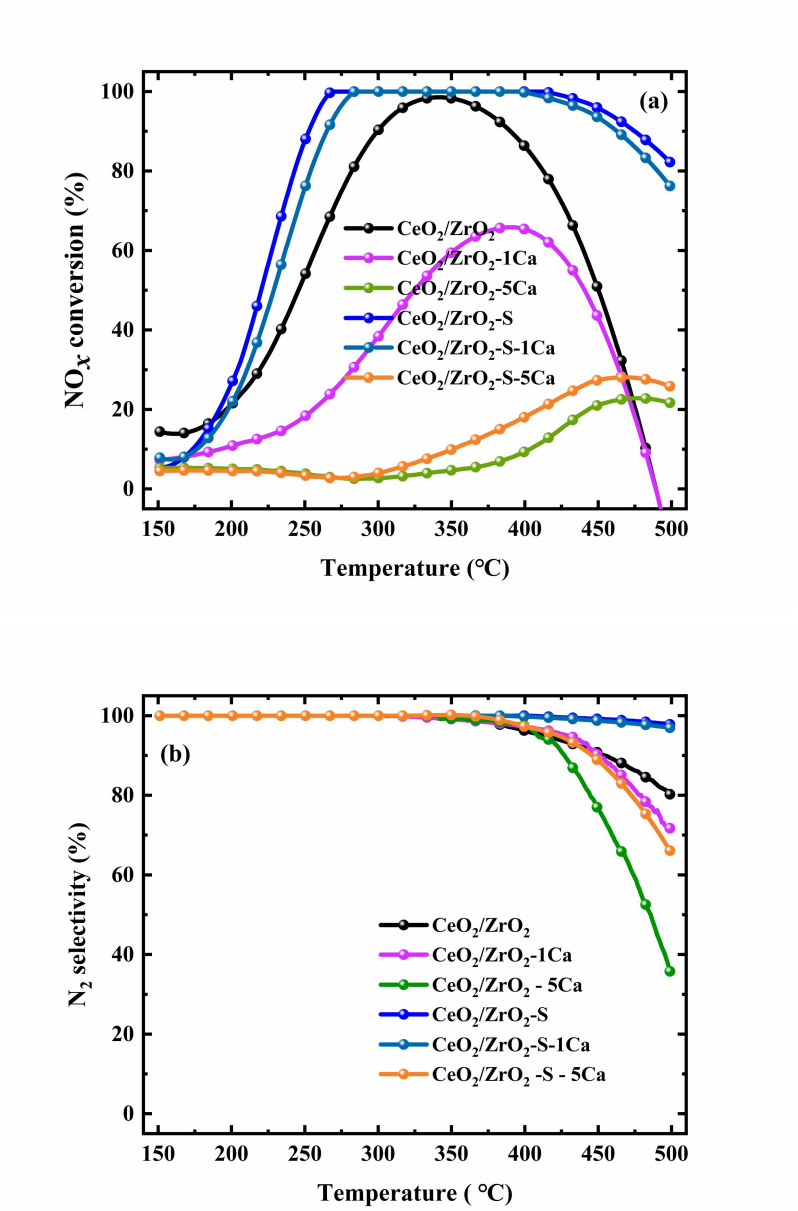
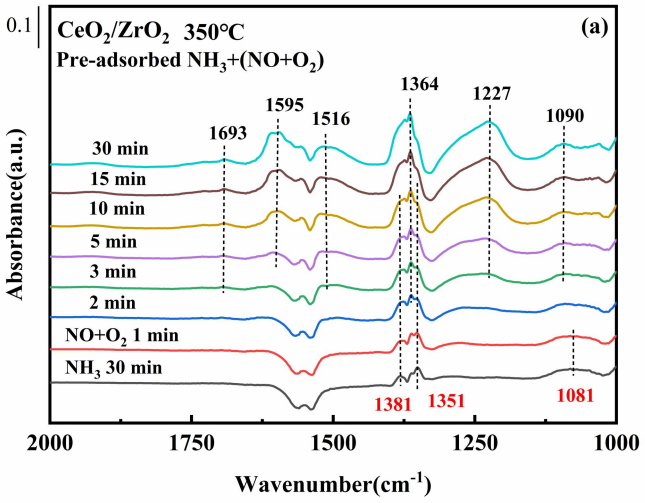
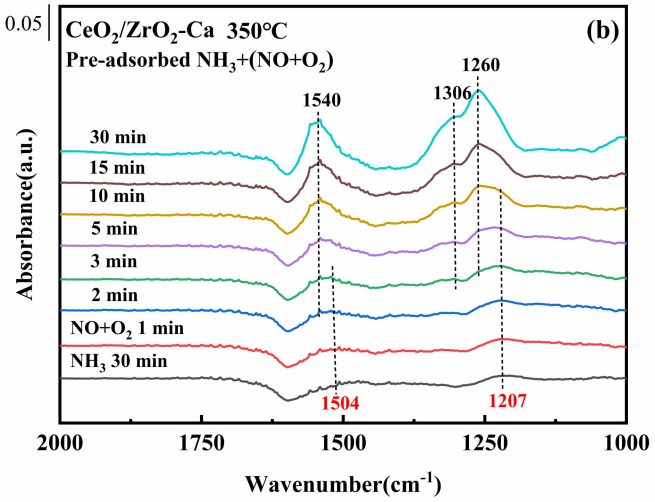
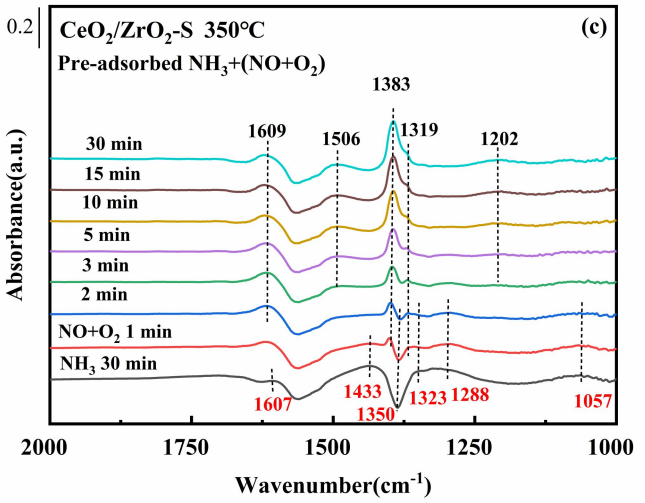


Fig. S1. SCR performance test results of CeO_2/ZrO_2, CeO_2/ZrO_2-1Ca, CeO_2/ZrO_2-5Ca, CeO_2/ZrO_2-S, CeO_2/ZrO_2-S-1Ca, CeO_2/ZrO_2-S-5Ca : (a), NO_x conversion; (b), N_2 selectivity.

Reaction conditions: 0.5 mL catalyst, [NO] = [NH_3] = 500 ppm, [O_2] = 5 vol.%, balance with N_2, total flow rate = 500 mL min^{-1} and GHSV =60,000 h^{-1}


0.1
CeO2/ZrO2 350°C
(a)
Pre-adsorbed NH3+(NO+O2)
1693
1595
1516
1364
1227
1090
30 min
15 min
10 min
5 min
3 min
2 min
NO+O2 1 min
NH3 30 min
1381
1351
1081
Absorbance(a.u.)
2000
1750
1500
1250
1000
Wavenumber(cm-1)


0.05
CeO2/ZrO2-Ca 350°C
(b)
Pre-adsorbed NH3+(NO+O2)
1540
1306
1260
30 min
15 min
10 min
5 min
3 min
2 min
NO+O2 1 min
NH3 30 min
1504
1207
Absorbance(a.u.)
2000
1750
1500
1250
1000
Wavenumber(cm-1)


0.2
CeO2/ZrO2-S 350°C
(c)
Pre-adsorbed NH3+(NO+O2)
1383
1609
1506
1319
1202
30 min
15 min
10 min
5 min
3 min
2 min
NO+O2 1 min
NH3 30 min
1607
1433
1350
1323
1288
1057
Absorbance(a.u.)
2000
1750
1500
1250
1000
Wavenumber(cm-1)

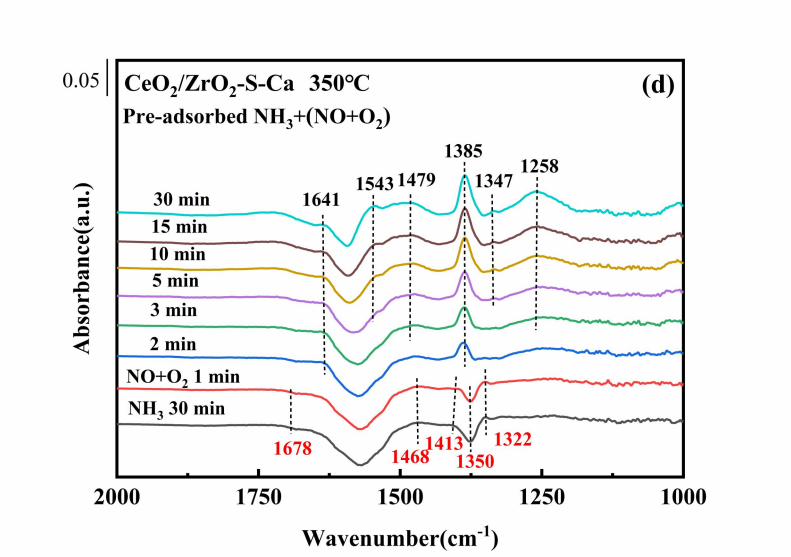
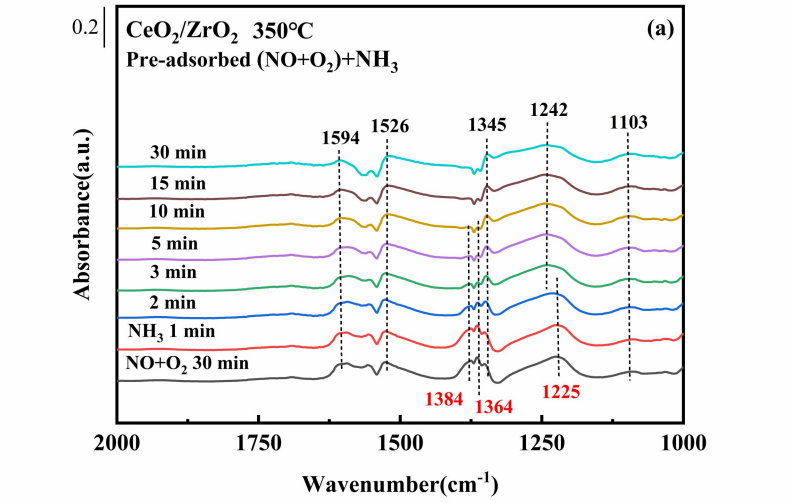
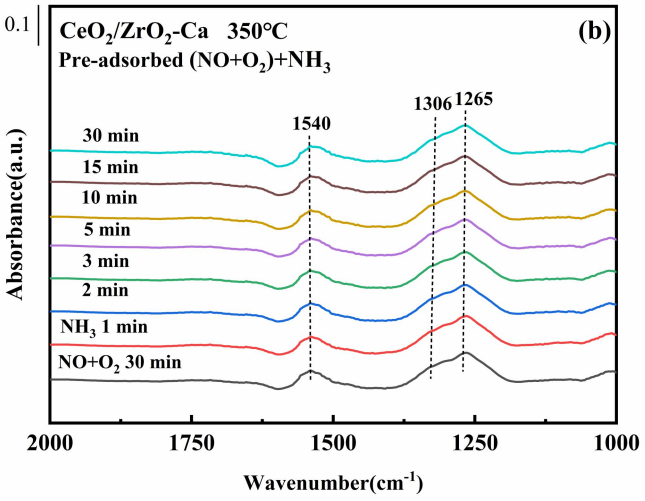
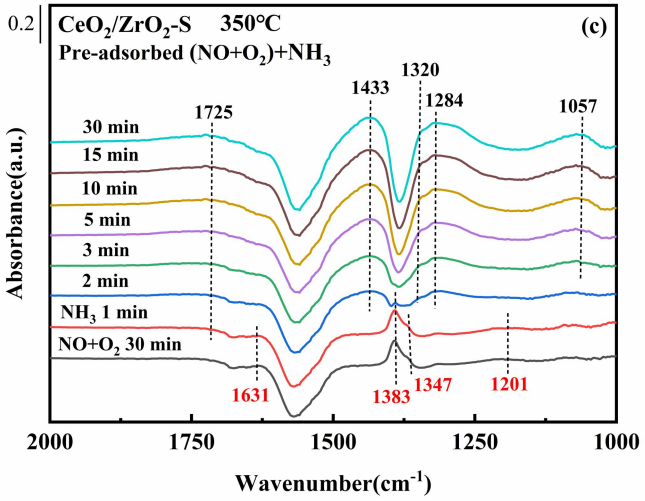


Fig. S2. In situ DRIFTS of reaction between NO + O_2 and adsorbed NH_3 species over (a) CeO_2/ZrO_2, (b) CeO_2/ZrO_2-Ca, (c) CeO_2/ZrO_2-S and (d) CeO_2/ZrO_2-S-Ca catalysts at 350 °C.




0.1
CeO2/ZrO2-Ca 350°C
(b)
Pre-adsorbed (NO+O2)+NH3
1540
1306
1265
30 min
15 min
10 min
5 min
3 min
2 min
NH3 1 min
NO+O2 30 min
Absorbance(a.u.)
2000
1750
1500
1250
1000
Wavenumber(cm-1)


0.2
CeO2/ZrO2-S 350°C
(c)
Pre-adsorbed (NO+O2)+NH3
1725
1433
1320
1284
1057
30 min
15 min
10 min
5 min
3 min
2 min
NH3 1 min
NO+O2 30 min
1631
1383
1347
1201
Absorbance(a.u.)
2000
1750
1500
1250
1000
Wavenumber(cm-1)

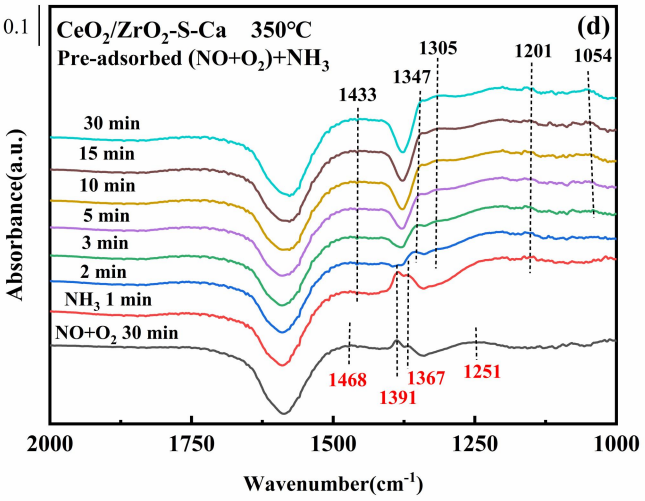

0.1
CeO2/ZrO2-S-Ca 350°C
(d)
Pre-adsorbed (NO+O2)+NH3
1433
1347
1305
1201
1054
30 min
15 min
10 min
5 min
3 min
2 min
NH3 1 min
NO+O2 30 min
1468
1391
1367
1251
Absorbance(a.u.)
2000
1750
1500
1250
1000
Wavenumber(cm-1)

Fig. S3. In situ DRIFTS of reaction between NH_3 and adsorbed $NO+O_2$ species over (a) CeO_2/ZrO_2, (b) CeO_2/ZrO_2-Ca, (c) CeO_2/ZrO_2-S and (d) CeO_2/ZrO_2-S-Ca catalysts at 350 ℃.