Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

A mixed catalyst prepared by mechanically milling VW/TiO_2 and low content of Pt/Al_2O_3 for SCO of high-concentration NH_3

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Table S1. Surface areas and average pore sizes of Pt/Al_2O_3, VW/TiO_2 and $Pt_{0.01}$@VW catalysts.

Sample	S_{BET} (m^2/g)	Pore volume (cm^2/g)	Pore diameter (nm)
Pt/Al_2O_3	154.78	0.79	18.53
VW/TiO_2	59.95	0.37	22.67
$Pt_{0.01}$@VW	59.06	0.31	19.37

Table S2. XPS results of Pt/Al_2O_3 and VW/TiO_2 catalysts

Sample	Pt (%)	V (%)	W (%)	O (%)	Al (%)	Ti (%)	$V^{4+}/V^{4+}+V^{5+}$ (%)	$O_\alpha/O_\alpha+O_\beta$ (%)	$O_\beta/O_\alpha+O_\beta$ (%)
Pt/Al_2O_3	1.36	-	-	60.65	37.99	-	-	15.58	84.42
VW/TiO_2	-	0.89	3.73	65.58	-	29.80	64.20	12.04	87.96

Table S3. Comparison of NH_3 conversion and N_2 selectivity of catalysts reported in literature and this work.

Catalyst	Preparation method	Reaction conditions	T_{100} (℃)	N_2 selectivity at T_{100} (%)	Ref.
$Pt_{0.01}$@VW (0.01 wt.% Pt)	**Impregnation and ball mill mixing**	**$[NH_3]$ = 5000 ppm, $[O_2]$ = 10 vol. %, N_2 as balance gas GHSV = 75,000 h^{-1}**	**300**	**84.3%**	**This work**
Pt/Al_2O_3 (0.46% wt.% Pt)	Impregnation	$[NH_3]$ = 500 ppm, $[O_2]$ = 5 vol. %, N_2 as balance gas GHSV = 66,000 h^{-1}	250	50	1
Pt/TiO_2 (0.1 wt.% Pt)	Wet impregnation	$[NH_3]$ = 2000 ppm, $[O_2]$ = 8 vol. %, N_2 as balance gas GHSV = 60,000 h^{-1}	275	48	2
$Pt/CeZrO_2$ (1 wt.% Pt)	Impregnation	$[NH_3]$ = 200 ppm, $[O_2]$ = 8 vol. %, N_2 as balance gas GHSV = 100,000 h^{-1}	330	42	3
PtCu/ZSM-5 (1.5 wt.% Pt)	Impregnation	$[NH_3]$ = 180 ppm, $[O_2]$ = 8 vol. %, N_2 as balance gas GHSV = 100,000 h^{-1}	275	72	4
$Pt/V/TiO_2$ (0.1 wt.% Pt)	Wet impregnation	$[NH_3]$ = 200 ppm, $[O_2]$ = 8 vol. %, N_2 as balance gas GHSV = 60,000 h^{-1}	250	50	5
$Pt-WO_3/ZrO_2$ (1.5 wt.% Pt)	Co-impregnation	$[NH_3]$ = 180 ppm, $[O_2]$ = 8 vol. %, N_2 as balance gas GHSV = 100,000 h^{-1}	300	58	6
Ag/nano-Al_2O_3	Impregnation	$[NH_3]$ = 500 ppm, $[O_2]$ = 10 vol. %, N_2 as balance gas GHSV = 28,000 h^{-1}	140	71	7

$Ag/SiO_2–TiO_2$ (10 wt.% Ag)	Impregnation	$[NH_3]$ = 500 ppm, $[O_2]$ = 10 vol. %, N_2 as balance gas GHSV = 28,000 h^{-1}	200	63	8
Ag/ZSM-5	Rotary evaporator	$[NH_3]$ = 1000 ppm, $[O_2]$ = 10 vol. %, N_2 as balance gas GHSV = 35,000 h^{-1}	135	75	9
Ag/Al_2O_3 (H_2 reduced)	Incipient wet impregnation	$[NH_3]$ = 500 ppm, $[O_2]$ = 10 vol. %, Ar as balance gas GHSV = 28,000 h^{-1}	180	83	10
CuO/Al_2O_3 (10 wt.% Cu)	Wet impregnation	$[NH_3]$ = 1000 ppm, $[O_2]$ = 10 vol. %, N_2 as balance gas GHSV = 50,000 h^{-1}	350	93	11
$CuO-Fe_2O_3$ (molar Cu:Fe = 1:1)	Sol-gel	$[NH_3]$ = 800 ppm, $[O_2]$ = 3 vol. %, N_2 as balance gas GHSV = 90,000 h^{-1}	250	91	12
$V_2O_5/CeO_2/TiO_2$ (10 wt.% Ce, 2 wt.% V)	Wet impregnation	$[NH_3]$ = 200 ppm, $[O_2]$ = 8 vol. %, N_2 as balance gas GHSV = 60,000 h^{-1}	300	90	13
$Fe_2O_3-TiO_2$ (5 wt.% Fe)	One–step sol–gel	$[NH_3]$ = 1000 ppm, $[O_2]$ = 3 vol. %, N_2 as balance gas GHSV = 200,000 h^{-1}	400	91	14
Mn_2O_3	Thermal decomposition	$[NH_3]$ = 500 ppm, $[O_2]$ = 3 vol. %, He as balance GHSV = 20,000 h^{-1}	210	60	15
MnO_2	Pelletized at high pressure	$[NH_3]$ = 500 ppm, $[O_2]$ = 3 vol. %, N_2 as balance GHSV = 20,000 h^{-1}	200	65	16
Mn-ZSM-5 (1.03 wt.% Mn)	Ion exchange	$[NH_3]$ = 1000 ppm, $[O_2]$ = 2 vol. %, N_2 as balance GHSV = 230,000 h^{-1}	350	77	17

Table S4 Pt mass fraction of mixed catalysts.

Mixed catalysts	Pt mass fraction / %
$Pt_{0.0025}$@VW	0.0025
$Pt_{0.005}$@VW	0.005
$Pt_{0.01}$@VW	0.01
$Pt_{0.02}$@VW	0.02

1. The stability test of $Pt_{0.01}$@VW catalyst

A long time experiment at 300 ℃ was conducted to evaluate the stability of $Pt_{0.01}$@VW catalyst, and the results are shown in Fig. S1. It could be seen that during 20 hours of experiment, the NH_3 conversion and N_2 selectivity of $Pt_{0.01}$@VW catalyst were always maintained at ~100% and ~84%, respectively. It indicated that $Pt_{0.01}$@VW catalyst had good stability.

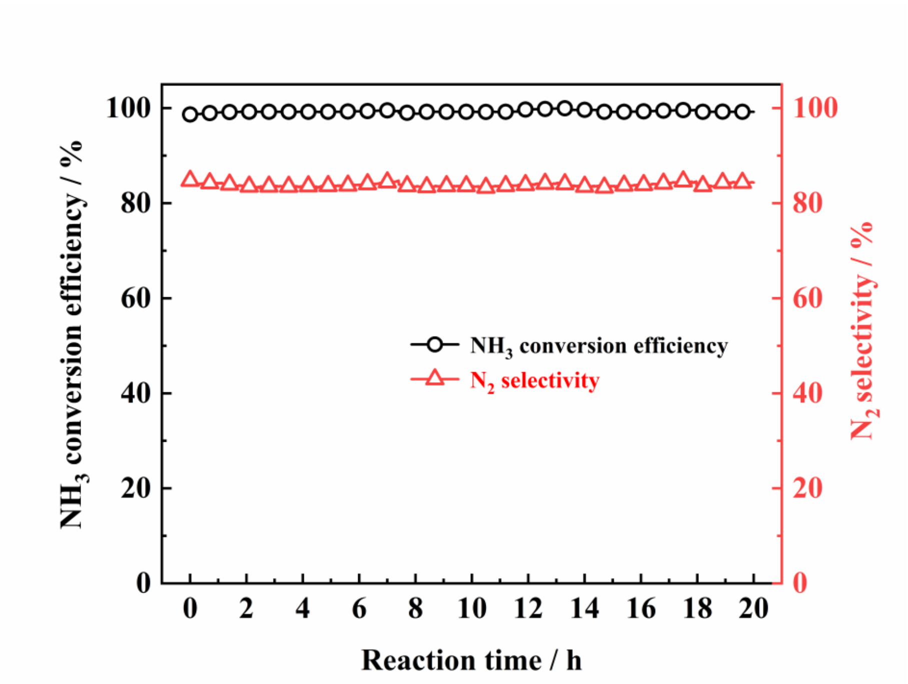


Fig. S1. NH_3 conversion efficiency and N_2 selectivity of $Pt_{0.01}$@VW catalyst at 300 ℃.

Reaction conditions: $[NH_3]_{in}$ = 5,000 ppm, $[O_2]_{in}$ = 10 vol%, GHSV = 75,000 h^{-1}, N_2 as balance gas.

2. The process of in-situ DRIFTS experiments

2.1. In-situ DRIFTS experiments of reaction between O_2 and pre-adsorbed NH_3

Firstly, catalysts were flushed by N_2 (100 mL/min) at 200 ℃. Then catalysts were pre-adsorbed with 5000 ppm of NH_3 (100 mL/min) for 30 min for saturation, and purged with N_2 (100 mL/min) for 30 min to eliminate physically adsorbed NH_3. Next, 10 % O_2 (100 mL/min) were introduced into the reactor, and the IR spectra were recorded as a function of time.

2.2. In-situ DRIFTS experiments of reaction between NH_3 and pre-adsorbed O_2

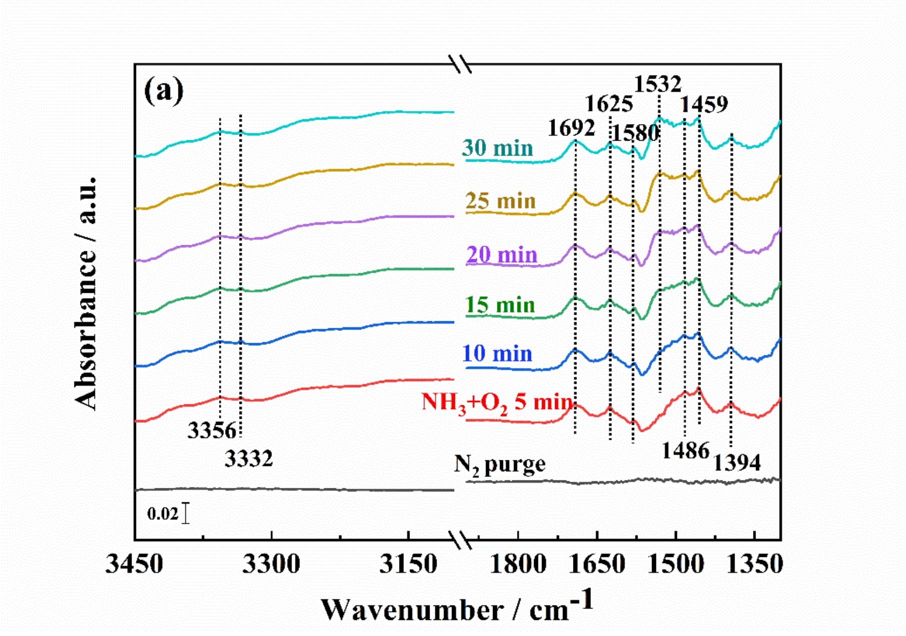
Firstly, catalysts were flushed by N_2 (100 mL/min) at 200 ℃. Then catalysts were pre-adsorbed with 10 % O_2 (100 mL/min) for 30 min for saturation, and purged with N_2 (100 mL/min) for 30 min to eliminate physically adsorbed O_2. Next, 5000 ppm NH_3 (100 mL/min) were introduced into the reactor. Then, the IR spectra were recorded as a function of time.

2.3. In-situ DRIFTS experiments of reaction between NH_3 and O_2

Firstly, catalysts were flushed by N_2 (100 mL/min) at 200 ℃. Then, 5000 ppm NH_3 (100 mL/min) were introduced into the reactor. Then, the IR spectra were recorded as a function of time.

3. The results of in-situ DRIFTS experiment of reaction between NH_3 and O_2

In-situ DRIFTS experiments in which NH_3 and O_2 were simultaneously introduced into reaction cell were carried out, and the results were shown in Fig. S2. As shown in Fig. R2(a), after the introduction of NH_3 and O_2, several IR bands appeared in the spectrum. With the increase of reaction time, the intensities of the bands which could be assigned to coordinated NH_3 on Lewis acid sites (3356, 3332 cm^{-1}) decreased slightly, while coordinated NH_3 on Lewis acid sites (1394 cm^{-1}), NH_4^+ species on Brønsted acid sites (1692, 1459 cm^{-1}), bridging nitrate species (1625,1257 cm^{-1}), monodentate nitrate species (1580, 1486 cm^{-1}) and $-NH_2$ species (1532 cm^{-1}) increased.[10-15] It indicated that coordinated NH_3 on Lewis acid sites was the intermediate in reaction between O_2 and NH_3 on Pt/Al_2O_3 catalyst surface. Similarly, it could be observed from Fig. S2 (b) that NH_4^+ species on Brønsted acid sites (1430, 1469 cm^{-1}) were involved in reaction of O_2 and NH_3 over VW/TiO_2 catalyst.[15,16] In the same way, Fig. S2(c) showed that NH_4^+ species on Brønsted acid sites (1436, cm^{-1}) and -OH species (1626 cm^{-1}) could participate the NH_3 oxidation reaction over $Pt_{0.01}$@VW catalyst.[17]



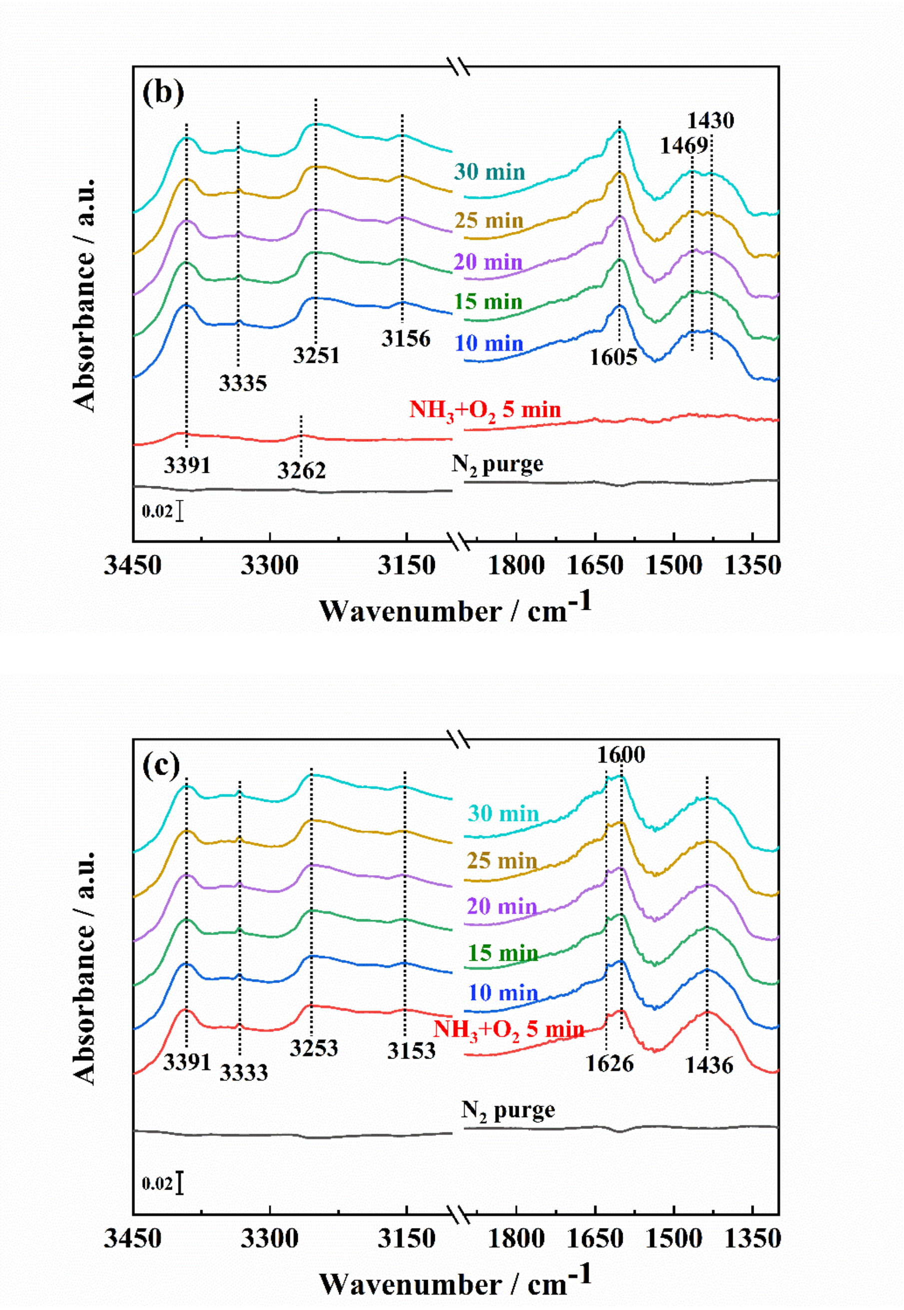


Fig. S2. In-situ DRIFT spectra of NH_3 reacting with O_2 over (a) Pt/Al_2O_3, (b) VW/TiO_2 and (c) $Pt_{0.01}$@VW catalysts at 300 ℃.

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