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Supplementary Information

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3 **Influence of Deposition Order of Dual Active Components on NH₃-SCO**
4 **performance of Bimetallic Pt-V System Supported on TiO₂**

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32 Section S1. Catalyst preparation

33 • $V_{0.5}/TiO_2$ catalyst

34 $V_{0.5}/TiO_2$ catalyst with 0.5 wt.% V was synthesized via wet impregnation method.²¹
35 Firstly, 0.554 g $C_2H_2O_4 \cdot 2H_2O$ (AR, 99.9 % purity, Sinopharm Chemical Reagent
36 Co.Ltd.) and 0.026 g NH_4VO_3 (AR, 99.95 % purity, Sinopharm Chemical Reagent
37 Co.Ltd.) were dissolved in 10 ml deionized water to prepare V precursor solution.
38 Then, 2 g TiO_2 powder (P25, Degussa, contains 79 wt.% anatase and 21 wt.% rutile)
39 was added to above solution, followed by stirring vigorously for 2 h at room
40 temperature. After that, the obtained suspension solution was initially dehydrated by
41 rotary evaporation, and further dried at 120 °C for 6 h. Finally, the obtained solid was
42 calcined at 500 °C for 3 h.

43 • $Pt_{0.04}V_{0.5}/TiO_2$ catalyst

44 The prepared method of $Pt_{0.04}V_{0.5}/TiO_2$ catalyst was similar to that of $V_{0.5}/TiO_2$
45 catalyst, except that 10 ml of diluted $Pt(NO_3)_2$ solution (AR, 18.02 wt. % Pt, Aladdin
46 Reagent Co.Ltd.) was added to V precursor solution before the addition of TiO_2
47 powder.

48 • $Pt_{0.04}/V_{0.5}/TiO_2$ catalyst

49 $Pt_{0.04}/V_{0.5}/TiO_2$ catalyst was prepared by impregnating $V_{0.5}/TiO_2$ catalyst in diluted
50 $Pt(NO_3)_2$ solution. Firstly, 2 g $V_{0.5}/TiO_2$ catalyst was added to 10 ml diluted $Pt(NO_3)_2$
51 solution, followed by stirring vigorously for 2 h at room temperature. Subsequently,
52 the obtained suspension solution was dehydrated by rotary evaporation, and further
53 dried at 120 °C for 6 h. Finally, the obtained solid was calcined at 500 °C for 3 h.

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55 Section S2. Catalyst characterization

56 The textural properties of catalysts were evaluated by using a physisorption
57 instrument (ASAP 2020 Plus, Micromeritics) at liquid nitrogen temperature (-196 °C).

58 The specific surface areas of catalysts were calculated by the N₂ adsorption-
59 desorption isotherm using Brunauer-Emmett-Teller (BET) equation. The average pore
60 diameter, pore volume and pore size distribution were calculated by the N₂ desorption
61 isotherm using Barrett-Joyner-Halenda (BJH) model.

62 The X-ray diffraction (XRD) test of catalysts were carried out on an X-ray diffraction
63 meter (Empyrean, PANalytical) using Cu K α ($\lambda=0.154$ nm) as radiation source. The
64 XRD diffractograms of catalysts were recorded in the 2θ range of 20-80 ° with a
65 scanning interval of 0.02 °.

66 X-ray photoelectron spectra (XPS) of catalysts were measured by using a
67 photoelectron spectrometer (AXIS-ULTRA DLD-600W, Shimadzu) with Al K α as
68 radiation source. The binding energies of different elements were calibrated by C 1s
69 peak at 284.6 eV.

70 Transmission electron microscopy (TEM) images of catalysts were measured on a
71 JEM-2100F electron microscope (JEOL, Japan). The acceleration voltage was 200
72 kV, and the surface chemical analysis was conducted by using energy dispersive X-
73 ray spectrometer (EDS).

74 The Raman spectra of prepared catalysts were performed at a Raman Spectrometer
75 (Jobin-Yvon LabRAM HR800), using an Ar ion laser (514.5 nm) as the excitation
76 source.

77 H₂-temperature programmed reduction (H₂-TPR), NH₃-temperature programmed
78 desorption (NH₃-TPD) and oxygen programmed desorption (O₂-TPD) were conducted
79 on a chemisorption analyzer (Autochem II 2920, Micromeritics). Before each H₂-TPR

80 test, sample was flushed in He stream (50 mL/min) at 300 °C for 30 min, and then
81 cooled down to 50 °C. The reduction reaction was proceed from 100 to 800 °C with a
82 heating rate of 10 °C/min. A mixture gas flow (50 mL/min) of 5 % H₂ and 95 % Ar
83 was used as reducing gas [19].

84 For NH₃-TPD experiments, each sample was pretreated in He stream (50 mL/min) for
85 30 min at 200 °C, and saturated with NH₃ at 50 °C for 1 h. Then, the sample was
86 treated by He stream at 50 °C for 1 h to eliminate physically absorbed NH₃. Finally,
87 the sample was heated from 100 to 800 °C at a ramping rate of 10 °C/min in He
88 stream (50 mL/min) and NH₃-TPD data were recorded in the meantime. During NH₃-
89 TPD experiments, the signals of reaction products N₂ (m/e = 28), N₂O (m/e = 44), NO
90 (m/e = 30), NO₂ (m/e = 46) and H₂ (m/e = 2) were recorded by using a quadrupole
91 mass spectrometer (QMS).

92 For O₂-TPD experiments, each sample was pretreated in He stream (50 mL/min) for
93 30 min at 200 °C, and saturated with O₂ at 50 °C for 1 h. Then, the sample was treated
94 by He stream at 50 °C for 1 h. Finally, the sample was heated from 100 to 900 °C at a
95 ramping rate of 10 °C/min in He stream (50 mL/min) and O₂-TPD data were recorded
96 at the same time.

97 The in-situ DRIFTS measurements were carried out on a FT-IR spectrometer (iS50,
98 Thermo Fisher Scientific) equipped with a reaction cell with KBr window (Praying
99 Mantis, Harrick) and a program temperature controller. Typically, samples were
100 pretreated in N₂ flow at 200 °C for 30 min, and then heated to specified temperature to
101 record the background spectra. Subsequently, in-situ DRIFTS spectra were recorded
102 after the reaction gas was introduced into reaction cell.

103 The processes of in-situ DRIFTS test using NH₃ as probe to characterize acid sites on
104 the surface of prepared catalysts were as follows: Firstly, catalysts were flushed by N₂

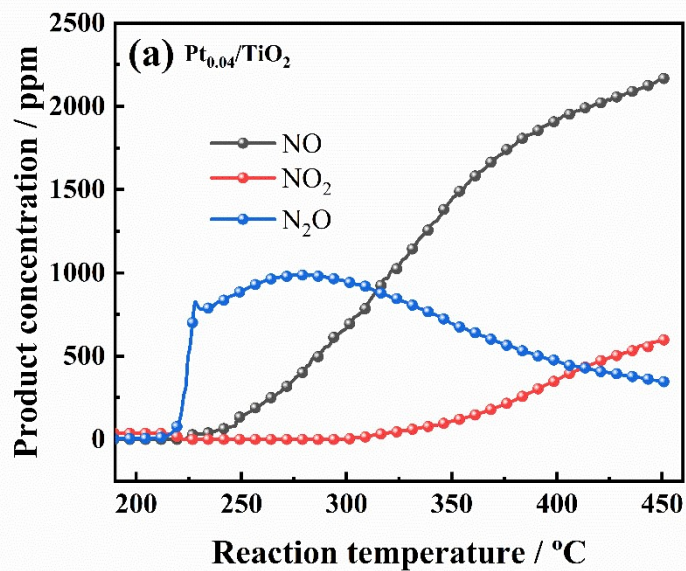
105 (100 mL/min) at 200 °C. Then catalysts were pre-adsorbed with 5000 ppm of NH₃
106 (100 mL/min) for 30 min for saturation, and purged with N₂ (100 mL/min) for 30 min
107 to eliminate physically adsorbed NH₃. Next, the IR spectra of NH₃ adsorption on the
108 surface of prepared catalysts were recorded.²¹

109 The in-situ DRIFTS experimental processes of reaction between O₂ and pre-adsorbed
110 NH₃ were as follows: Firstly, catalysts were flushed by N₂ (100 mL/min) at 200 °C.
111 Then catalysts were pre-adsorbed with 5000 ppm of NH₃ (100 mL/min) for 30 min for
112 saturation, and purged with N₂ (100 mL/min) for 30 min to eliminate physically
113 adsorbed NH₃. Next, 10 % O₂ (100 mL/min) were introduced into the reactor, and the
114 IR spectra were recorded as a function of time.²¹

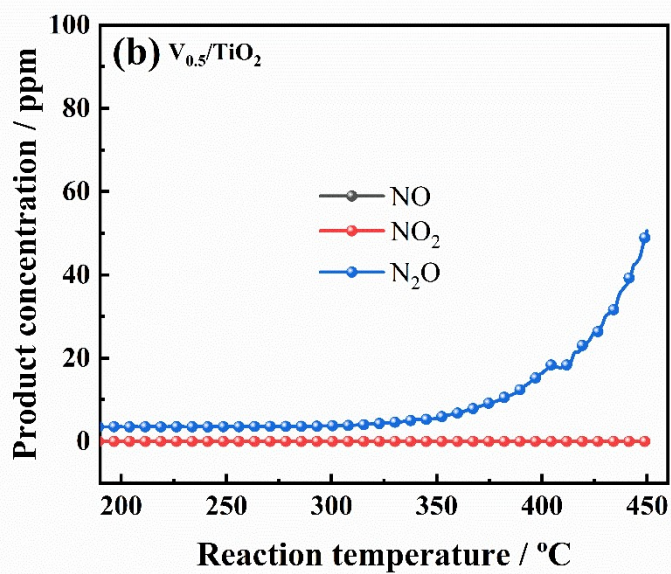
115 The in-situ DRIFTS experimental processes of reaction between NH₃ and pre-
116 adsorbed O₂ were as follows: Firstly, catalysts were flushed by N₂ (100 mL/min) at
117 200 °C. Then catalysts were pre-adsorbed with 10 % O₂ (100 mL/min) for 30 min for
118 saturation, and purged with N₂ (100 mL/min) for 30 min to eliminate physically
119 adsorbed O₂. Next, 5000 ppm NH₃ (100 mL/min) were introduced into the reactor.
120 Then, the IR spectra were recorded as a function of time.²¹

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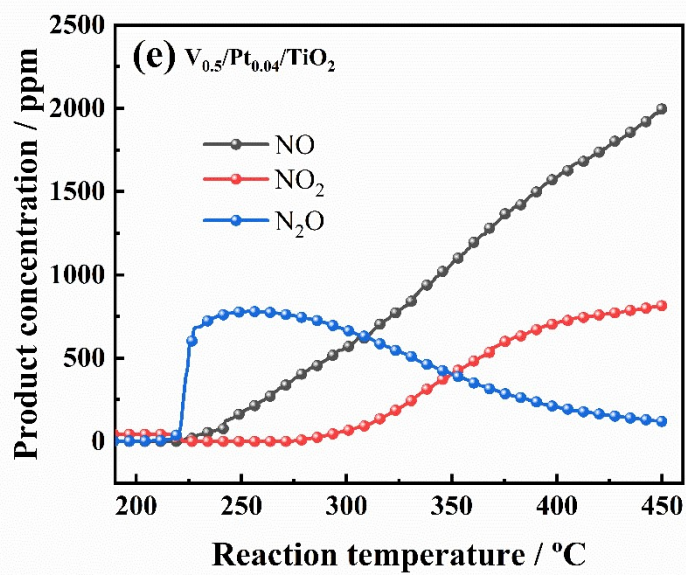
122 Section S3. The changes of NO_x concentration during the activity test of
123 prepared catalysts.



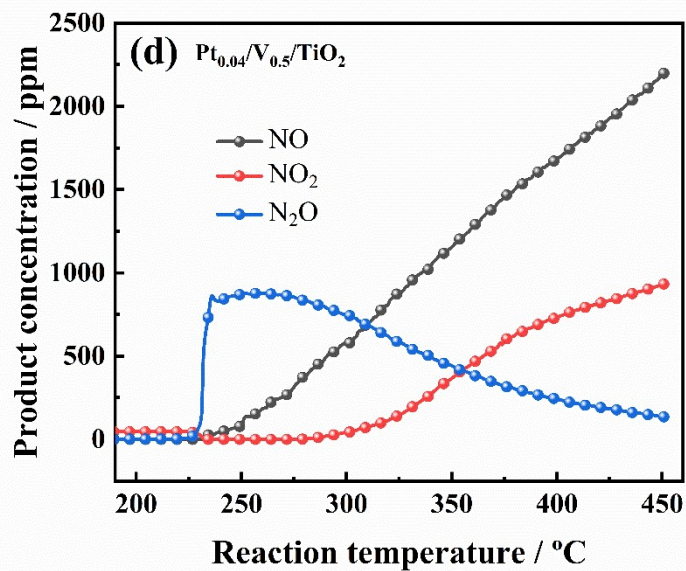
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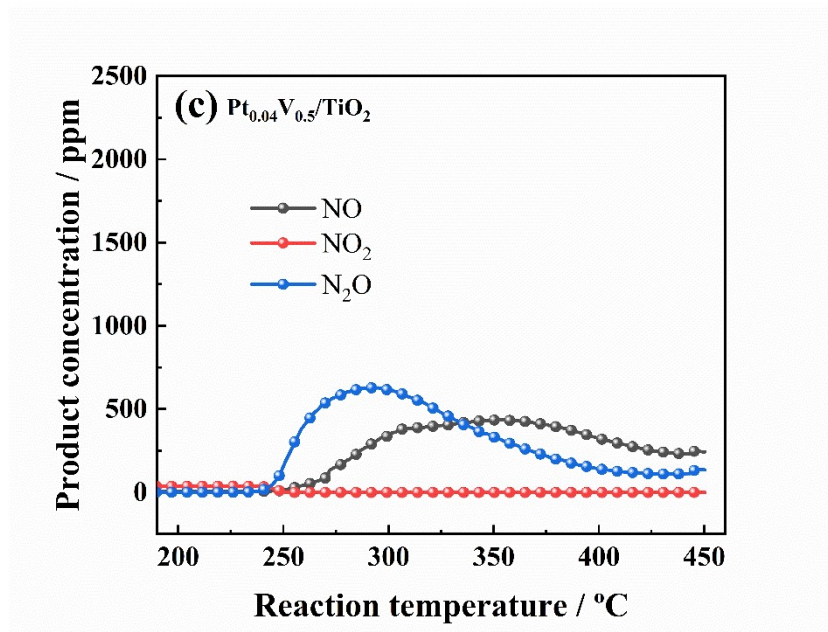
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131 Fig. S1. The changes of NO_x concentration during the activity test of (a) $\text{Pt}_{0.04}/\text{TiO}_2$,

132 (b) $\text{V}_{0.5}/\text{TiO}_2$, (c) $\text{V}_{0.5}/\text{Pt}_{0.04}/\text{TiO}_2$, (d) $\text{Pt}_{0.04}/\text{V}_{0.5}/\text{TiO}_2$, (e) $\text{Pt}_{0.04}\text{V}_{0.5}/\text{TiO}_2$ catalysts.

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134 **Section S4. The comparison of NH₃-SCO performance of catalysts**

135 The comparison of NH₃-SCO performance of catalysts in previous work and

136 V_{0.5}/Pt_{0.04}/TiO₂ catalyst in this work was shown in Table S1. T₁₀₀ represents the

137 corresponding reaction temperature when NH₃ removal efficiency was 100 %.

138 Table S1. The comparison of catalysts in previous work and V_{0.5}/Pt_{0.04}/TiO₂ catalyst

139 in this work.

Catalyst	Synthesis process	Experimental conditions	T ₁₀₀ (°C)	N ₂ selectivity at T ₁₀₀ (%)	Ref.
V_{0.5}/Pt_{0.04}/TiO₂ (0.04 wt.% Pt)	Impregnation	NH₃ : 5000 ppm O₂ : 10 vol. % N₂ as balance gas GHSV : 75,000 h⁻¹	225	80.2%	This work
Pt/TiO ₂ (0.1 wt.% Pt)	impregnation	NH ₃ : 2000 ppm O ₂ : 8 vol. % N ₂ as balance gas GHSV : 60,000 h ⁻¹	275	48	1
PtVW/TiO ₂ (0.1 wt.% Pt)	impregnation	NH ₃ : 200 ppm O ₂ : 5 vol. % N ₂ as balance gas GHSV : 100,000 h ⁻¹	250	50	2
Pt-WO ₃ /ZrO ₂ (1.5 wt.% Pt)	Impregnation	[NH ₃] = 180 ppm, [O ₂] = 8 vol. %, N ₂ as balance gas GHSV = 100,000 h ⁻¹	300	58	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/Al ₂ O 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	5
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	6
Pt-ZSM-5 (2.55 wt.% Pt)	Ion-exchange	[NH ₃] = 1000 ppm, [O ₂] = 4 vol. %, N ₂ as balance gas GHSV = 50,000 h ⁻¹	200	71	7
V ₂ O ₅ /TiO ₂ (2 wt.% V ₂ O ₅)	Mortar mixing of powders	[NH ₃] = 800 ppm, [O ₂] = 3 vol. %, Ar as balance gas GHSV = 60,000 h ⁻¹	250	82	8
V ₂ O 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	9
Ag/nano-Al ₂ O ₃	Impregnation	[NH ₃] = 500 ppm, [O ₂] = 10 vol. %, N ₂ as balance gas GHSV = 28,000 h ⁻¹	140	71	10
Ag/Al ₂ O 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	11

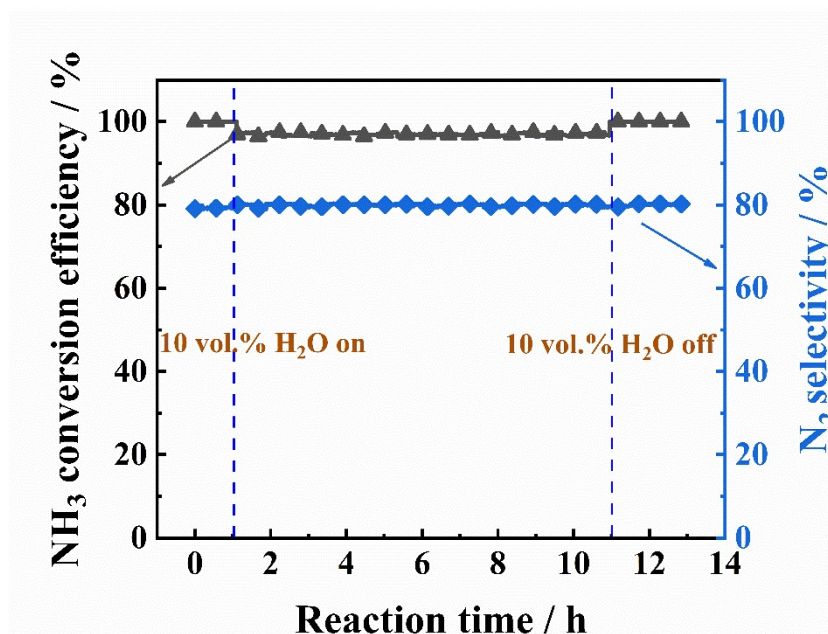
Ag/SiO ₂ -TiO ₂ (10 wt.% Ag)	Impregnation	[NH ₃] = 500 ppm, [O ₂] = 10 vol. %, N ₂ as balance gas GHSV = 28,000 h ⁻¹	200	63	12
Ag/ZSM-5	Rotary evaporator	[NH ₃] = 1000 ppm, [O ₂] = 10 vol. %, N ₂ as balance gas GHSV = 35,000 h ⁻¹	135	75	13
CuO/Al ₂ O ₃ (10 wt.% Cu)	Wet impregnation	[NH ₃] = 1000 ppm, [O ₂] = 10 vol. %, N ₂ as balance gas GHSV = 50,000 h ⁻¹	350	93	14
CuO-Fe ₂ O 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	15
Fe ₂ O 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	16
Mn ₂ O ₃	Thermal decomposition	[NH ₃] = 500 ppm, [O ₂] = 3 vol. %, He as balance GHSV = 20,000 h ⁻¹	210	60	17
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	18

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142 **Section S5. The results of H₂O resistance test**

143 H₂O resistance test of V_{0.5}/Pt_{0.04}/TiO₂ catalyst was performed at 225 °C, and the
144 results were shown in Fig. S2. As shown in Fig. S2, after the injection of 10 vol.%
145 H₂O vapor, the NH₃ conversion efficiency of V_{0.5}/Pt_{0.04}/TiO₂ catalyst slightly
146 decreased from 100 % to ~97.7 %, and the N₂ selectivity changed little. When H₂O
147 vapor was cut off, the NH₃ conversion efficiency returned to 100 % rapidly, and the
148 N₂ selectivity did not change obviously. This indicated that V_{0.5}/Pt_{0.04}/TiO₂ catalyst
149 possessed good H₂O resistance, and the slight deactivation of V_{0.5}/Pt_{0.04}/TiO₂ catalyst
150 caused by H₂O introduction was reversible.



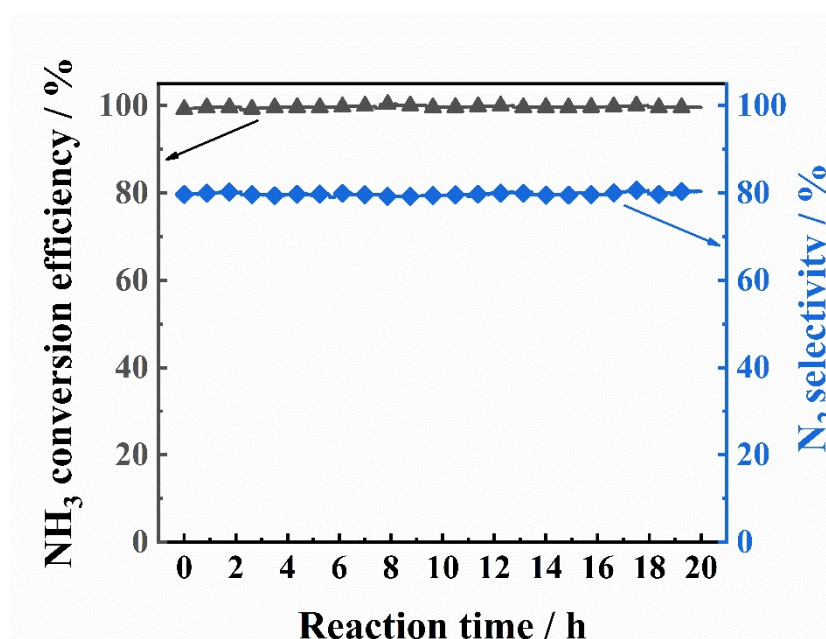
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152 Fig. S2. H₂O resistance test results of V_{0.5}/Pt_{0.04}/TiO₂ catalyst at 225 °C.

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154 **Section S6. The results of activity stability test**

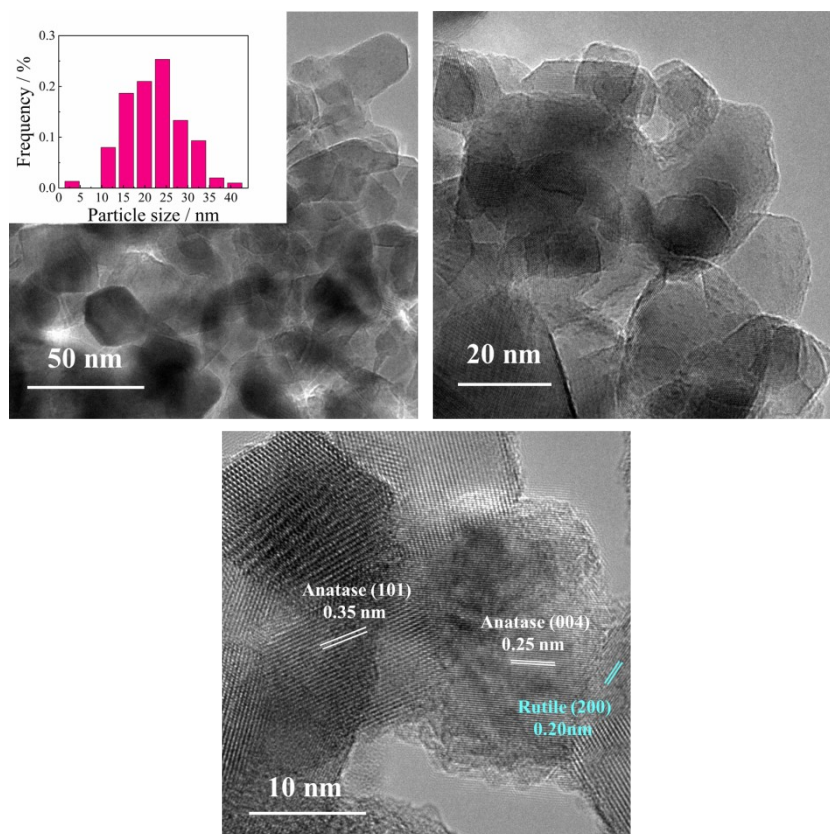
155 Aiming to test the activity stability of $V_{0.5}/Pt_{0.04}/TiO_2$ catalyst, a 20-hour stability test
156 was carried out, and the results were shown in Fig. S3. It could be seen that during 20
157 hours of test, the NH_3 conversion and N_2 selectivity of $V_{0.5}/Pt_{0.04}/TiO_2$ catalyst were
158 maintained at $\sim 100\%$ and $\sim 80\%$, respectively. It indicated that $V_{0.5}/Pt_{0.04}/TiO_2$
159 catalyst possessed good stability.



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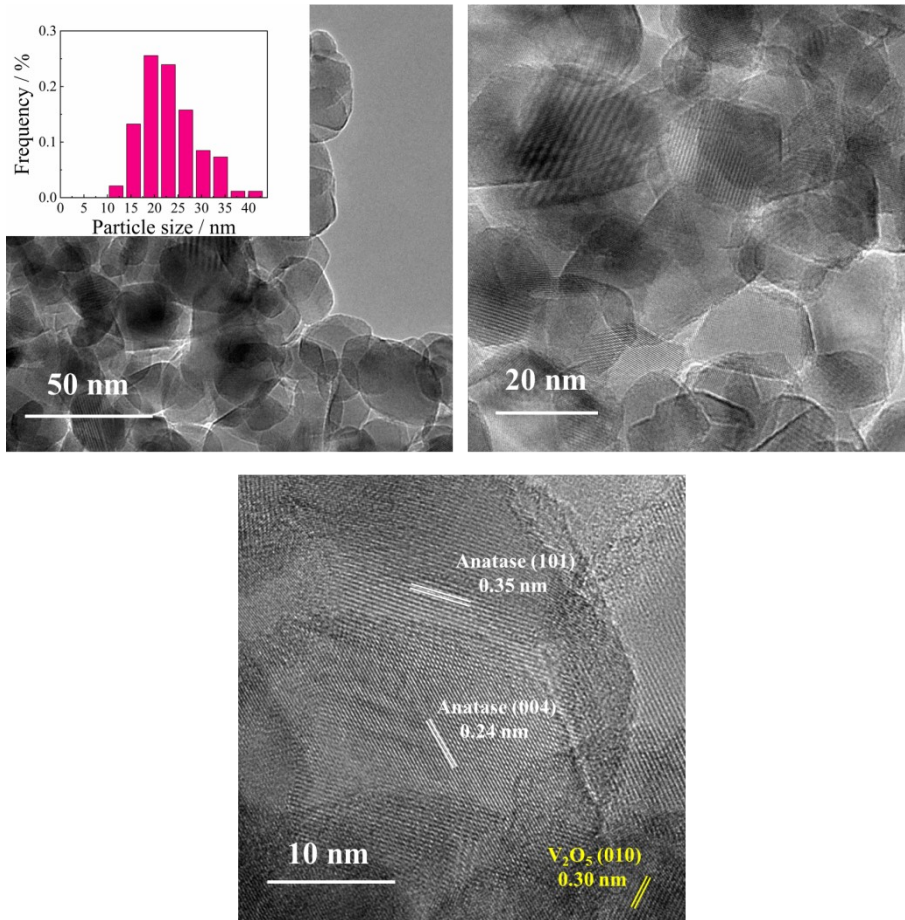
161 Fig. S3. Stability test results of $V_{0.5}/Pt_{0.04}/TiO_2$ catalyst at 225 °C.

162 Section S7. HRTEM results



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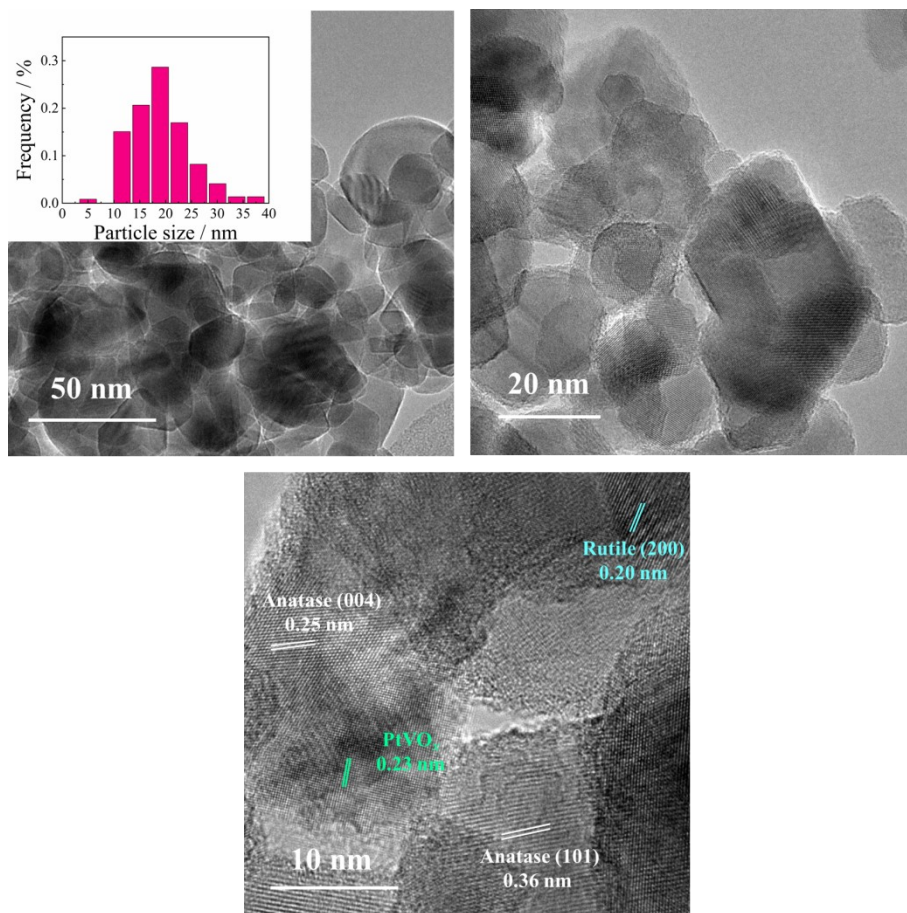
Fig. S4. HRTEM images of Pt_{0.04}/TiO₂ catalyst.



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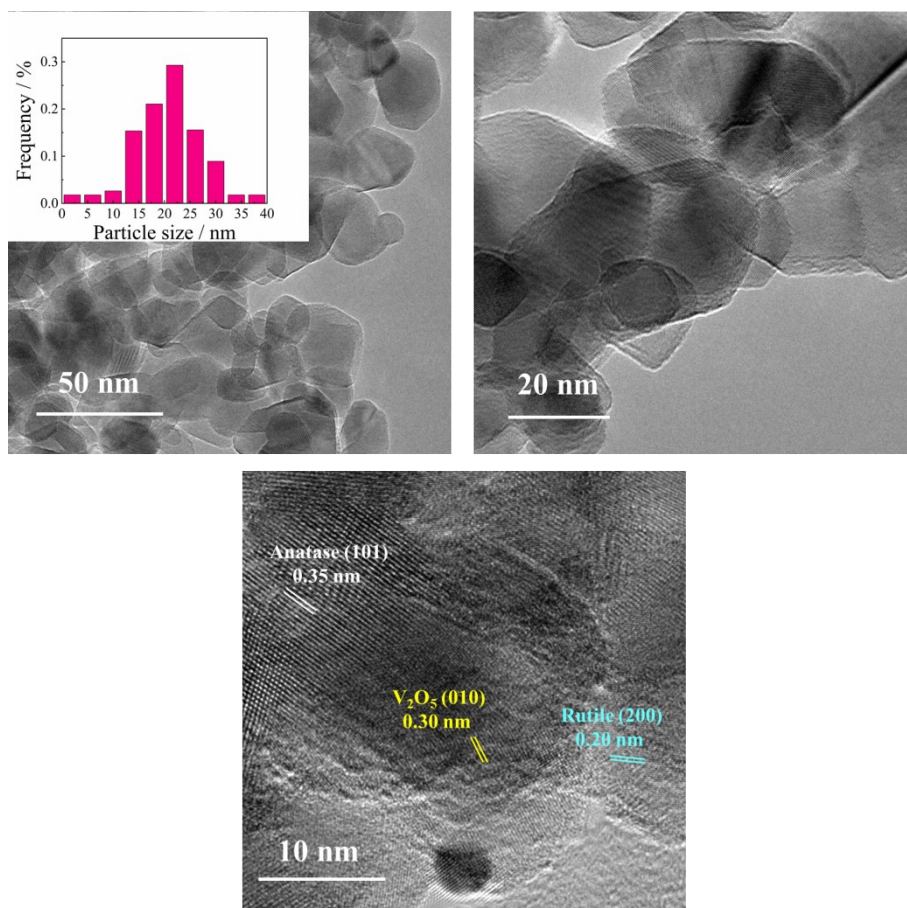
Fig. S5. HRTEM images of $V_{0.5}/TiO_2$ catalyst.



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Fig. S6. HRTEM images of $\text{Pt}_{0.04}\text{V}_{0.5}/\text{TiO}_2$ catalyst.

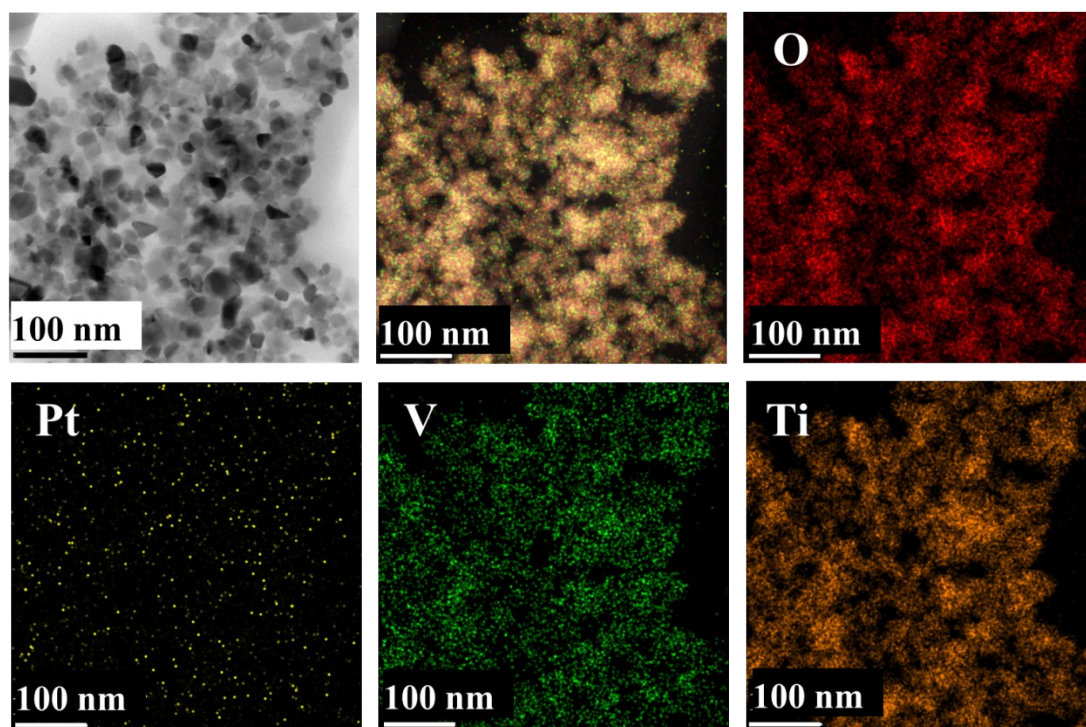


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Fig. S7. HRTEM images of $\text{Pt}_{0.04}/\text{V}_{0.5}/\text{TiO}_2$ catalyst.

171 **Section S8. EDS mapping results**



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Fig. S8. EDS mappings of $\text{Pt}_{0.04}/\text{V}_{0.5}/\text{TiO}_2$ catalyst.

174 **Section S9. N_2 adsorption and desorption and XPS data**

175 Table S2. Specific surface areas and average pore sizes of prepared catalysts.

Sample	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
$\text{Pt}_{0.04}/\text{TiO}_2$	52.21	0.32	21.38
$\text{V}_{0.5}/\text{TiO}_2$	57.16	0.41	25.40
$\text{V}_{0.5}/\text{Pt}_{0.04}/\text{TiO}_2$	50.36	0.33	23.72
$\text{Pt}_{0.04}/\text{V}_{0.5}/\text{TiO}_2$	50.60	0.33	22.75
$\text{Pt}_{0.04}\text{V}_{0.5}/\text{TiO}_2$	49.81	0.34	23.32

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Table S3. XPS results of prepared catalysts

Sample	Pt (%)	V (%)	O (%)	$V^{3+}/V^{3+}+V^{4+}+V^{5+}$ (%)	$V^{4+}/V^{3+}+V^{4+}+V^{5+}$ (%)	$O_{\alpha}/O_{\alpha}+O_{\beta}$ (%)	$Pt^0/Pt^0+Pt^{2+}+Pt^{4+}$ (%)	$Pt^{2+}/Pt^0+Pt^{2+}+Pt^{4+}$ (%)	$Pt^{4+}/Pt^0+Pt^{2+}+Pt^{4+}$ (%)
Pt _{0.04} /TiO ₂	0.16	-	66.60	-	-	13.28	39.97	27.20	32.83
V _{0.5} /TiO ₂	-	17.91	55.55	28.87	44.26	16.62	-		
V _{0.5} /Pt _{0.04} /TiO ₂	0.10	1.25	66.60	38.75	28.88	20.73	35.56	33.13	31.31
Pt _{0.04} /V _{0.5} /TiO ₂	0.15	1.20	66.75	24.50	40.60	20.09	16.22	67.35	16.43
Pt _{0.04} V _{0.5} /TiO ₂	0.12	1.15	66.03	28.72	38.98	19.22	17.42	60.25	22.33

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