Supporting Information

Structure-Activity Relationships of Hydrothermally Aged Titania-Supported Vanadium-Tungsten Oxide Catalysts for SCR of NO_x Emissions with NH_3

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Table S1. ICP of vanadium content in catalysts. Wt.% V was converted to wt.%V_2O_5 by adding 2.5 O per detected V atom.

Sample	**% Vanadium**	**% V_2O_5**
1% V_2O_5-1%WO_3/TiO_2-650	0.54	0.97
1% V_2O_5-1%WO_3/TiO_2-HTA650	0.52	0.94
1% V_2O_5-5%WO_3/TiO_2-650	0.45	0.81
1% V_2O_5-5%WO_3/TiO_2-HTA650	0.44	0.78
1% V_2O_5-8%WO_3/TiO_2-650	0.45	0.80
1% V_2O_5-8%WO_3/TiO_2-HTA650	0.43	0.76

Table S2. The calculated crystallite sizes (Scherrer equation) for supported VWTi catalysts treated at 650°C.

Samples	% Rutile	% Anatase	Crystal size (nm)	
			Anatase	Rutile
Calcined 1V1WTi	23	77	21	21
Hydrothermally aged 1V1WTi	42	58	23	28
Calcined 1V8WTi	19	81	18	24
Hydrothermally aged 1V8WTi	28	72	19	25

Table S3. Vanadium wt.% present as reduced V^{+4} determined by EPR line integration.

Catalysts	**V wt.% as V^{+4}**
1V1WTi-650°C	8%
1V1WTi-HTA-650°C	7%
1V5WTi-650°C	15%
1V5WTi-HTA-650°C	7%
1V8WTi-650C	16%
1V8WTi-HTA-650°C	13%

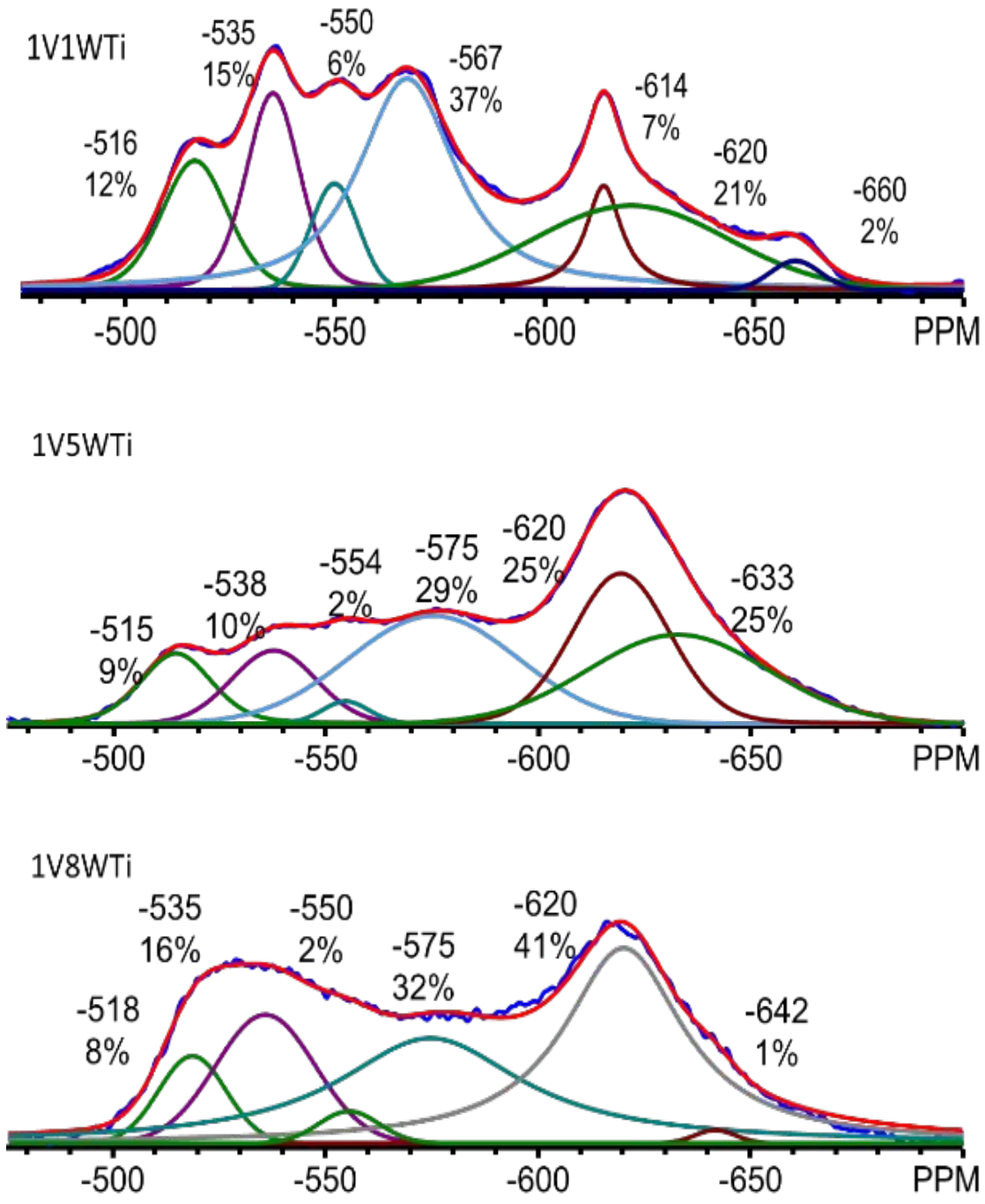


Figure S1. Solid-state ^{51}V MAS NMR spectra of dehydrated supported V_2O_5-WO_3/TiO_2 catalysts calcined at 650°C.

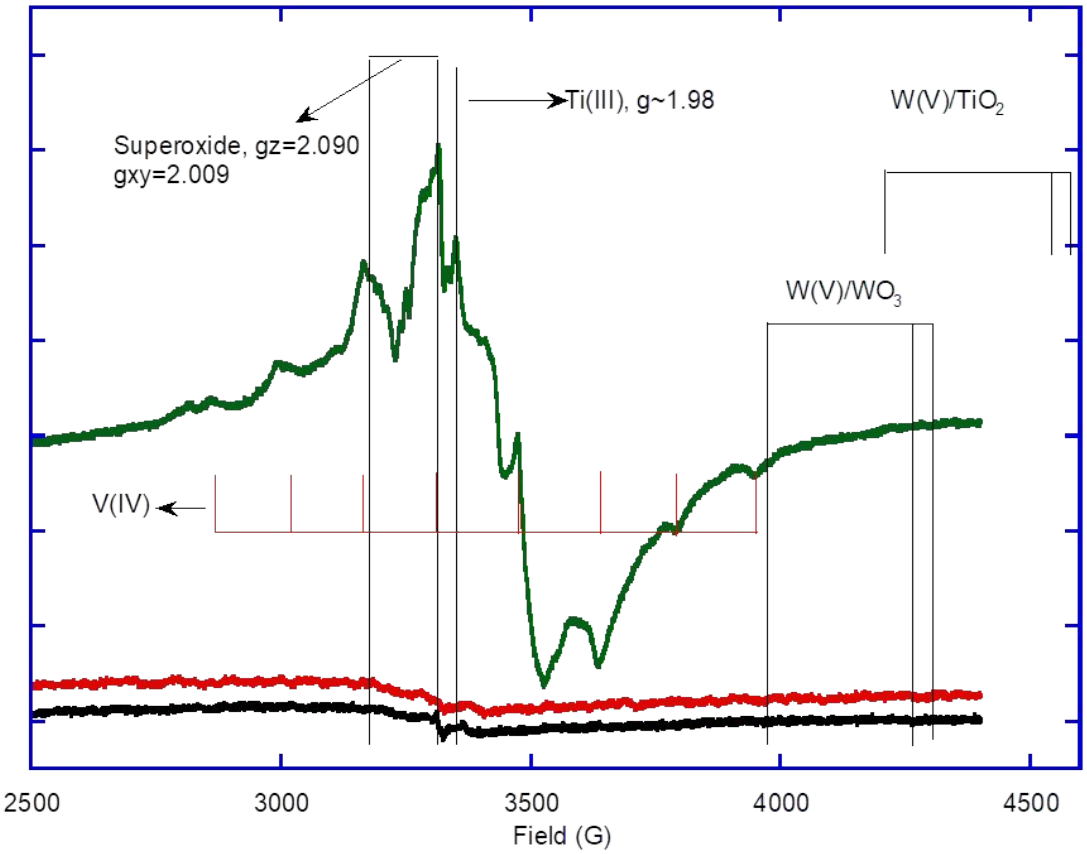
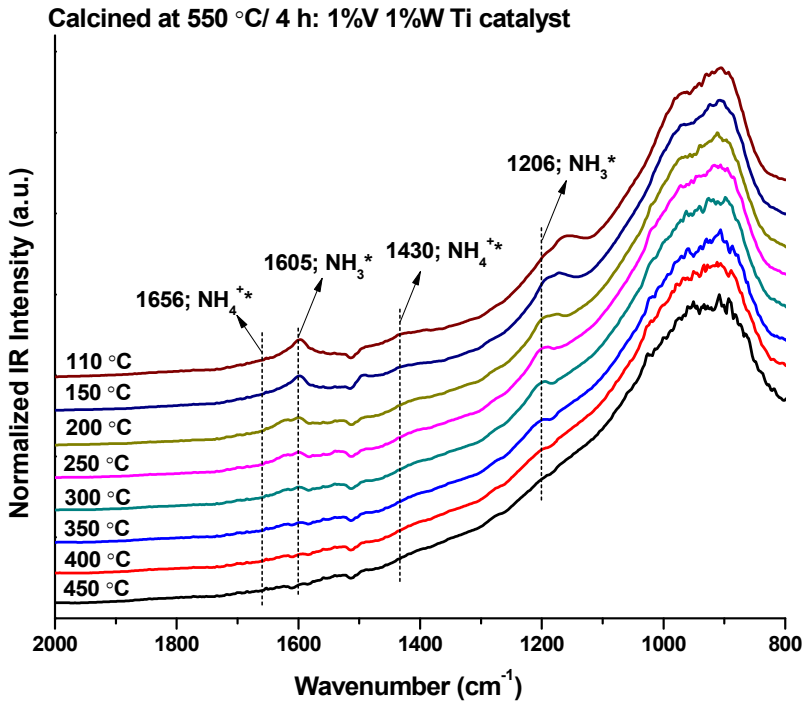


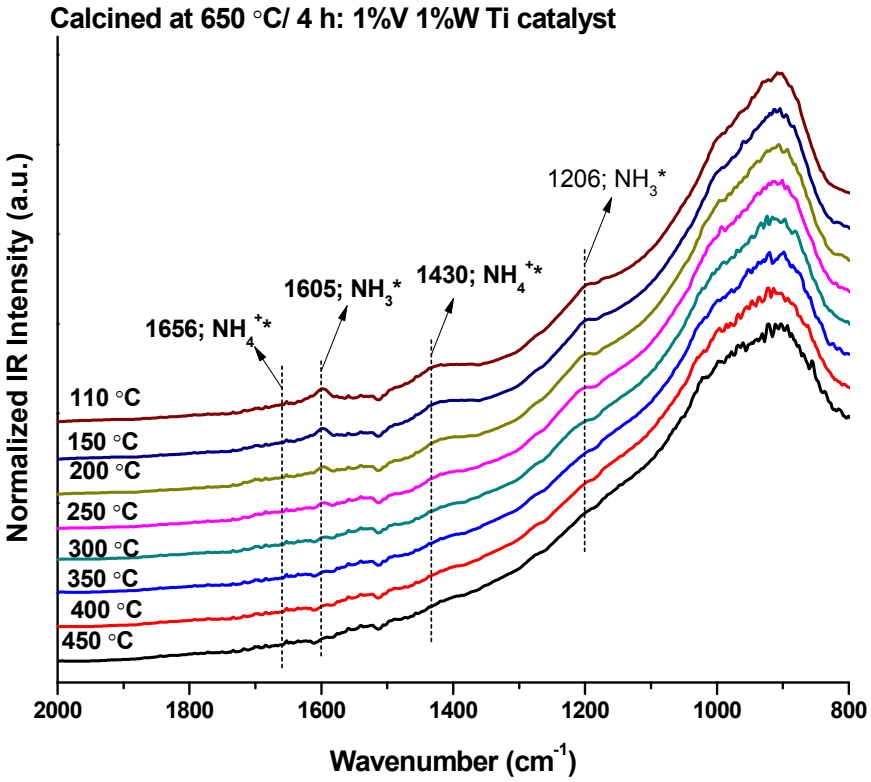
Figure S2. EPR spectra at 125 K showing positions of non-vanadium species. TiO_2 as received (Black), TiO_2 calcined at 650 C, 1W 1V TiO_2 calcined at 650 C. Black lines are positioned at the field positions corresponding to g values for the indicated species.

Potential overlapping EPR spectra from Ti(III), superoxide and W(V)
Multiple previous researchers have failed to find evidence of EPR spectra from W(+5) in W/V TiO2.[1-3] The spectrum of W(+5) was reported for rutile by Chang,[4] and similar to other instances of W(+5) in inorganic solids such as oxides,[5] it displays g values considerably lower than the free electron g of 1.44, 1.57 and 1.47, if the species was in a WO_3 cluster, a report of W(+5) in WO_3 yielded 1.55, 1.68 and 1.56 for g values.[6] Additionally, the relaxation for these species was reported to be rapid, with all spectra collected at 20 K or lower. A spectrum of 1W1V 650C was obtained at 6K (not shown), and only spectra corresponding to superoxide and V(IV) were seen.

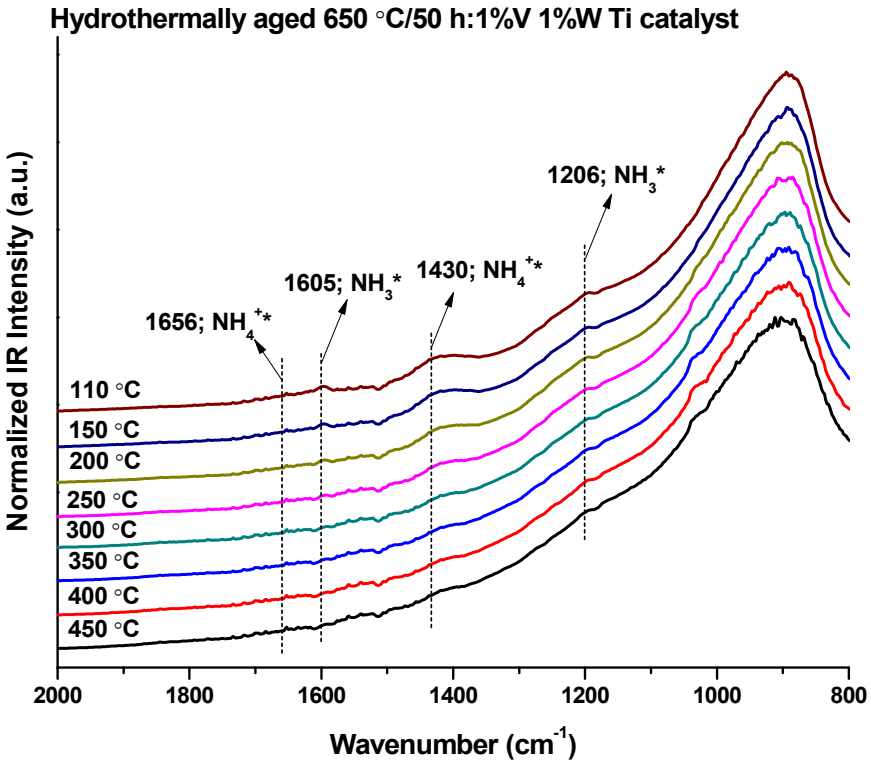
A) 550°C Calcined: 1%V_2O_5 – 1%WO_3/TiO_2



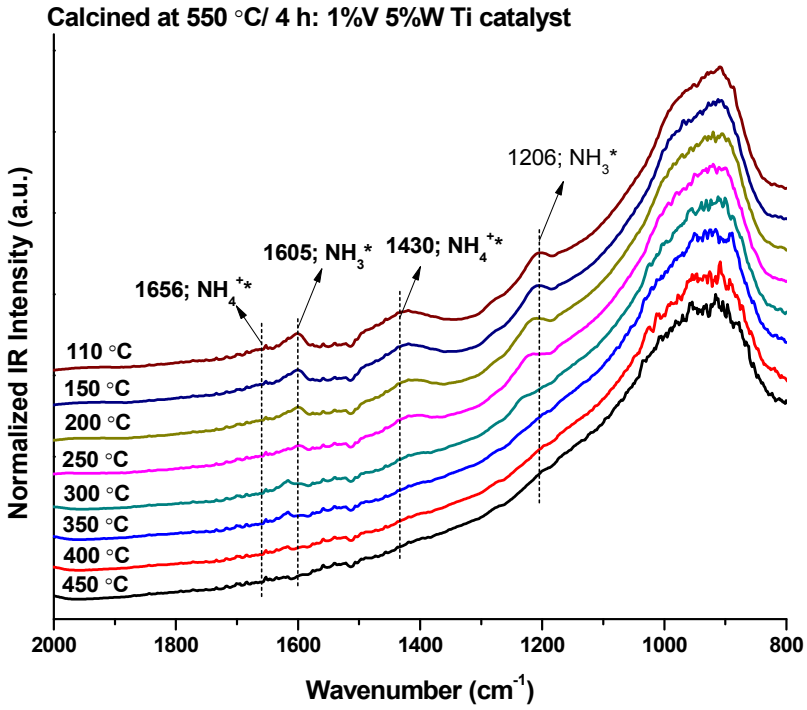
B) 650°C Calcined: 1%V_2O_5 – 1%WO_3/TiO_2



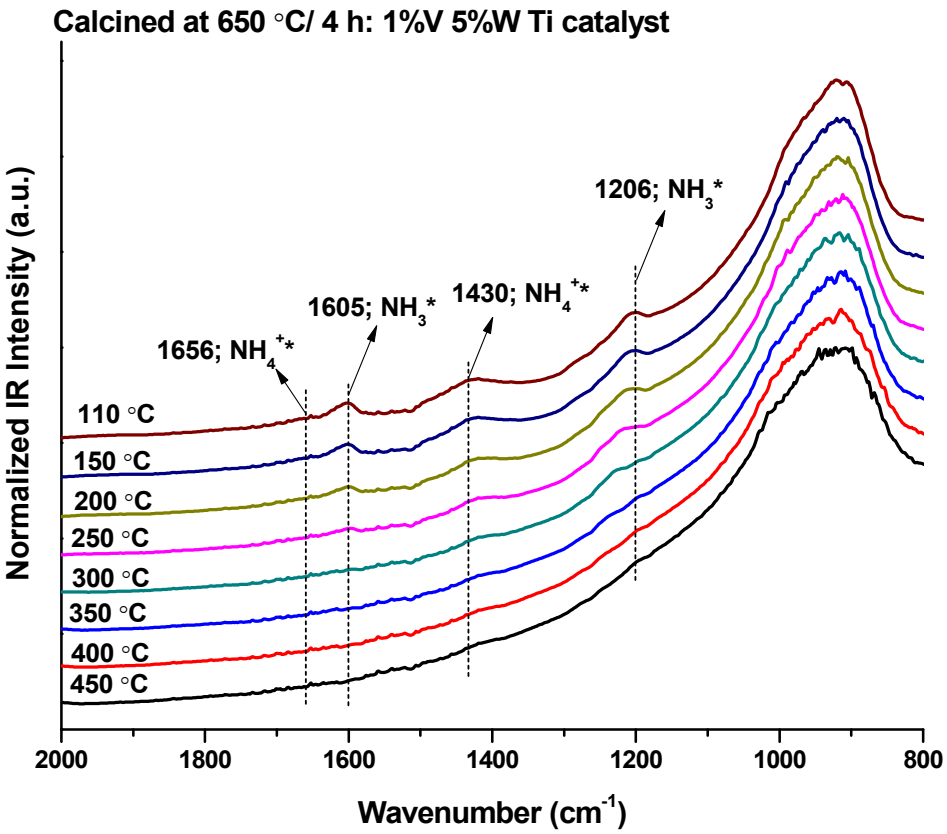
C) 650°C Hydrothermally aged: 50 hr 1%V_2O_5 – 1%WO_3/TiO_2



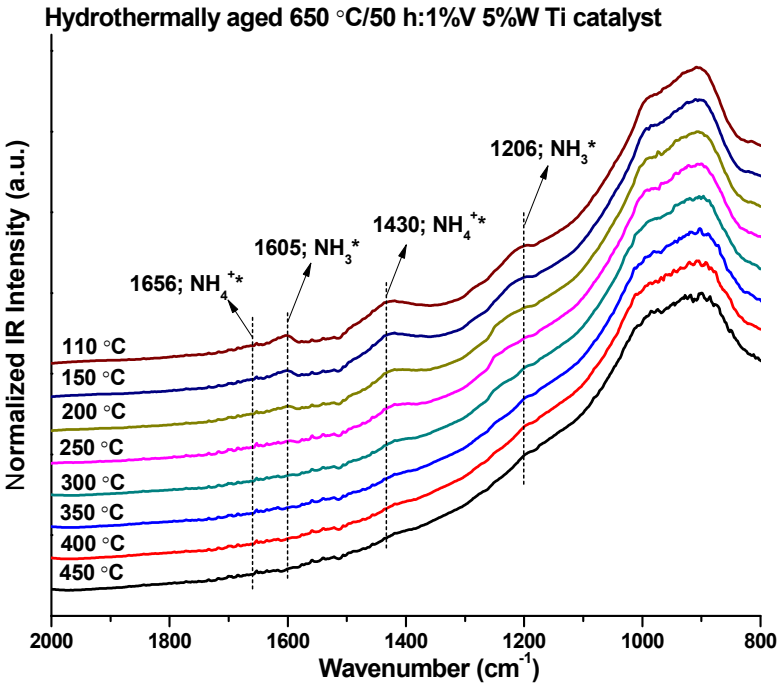
D) 550°C Calcined: 1%V_2O_5 – 5%WO_3/TiO_2



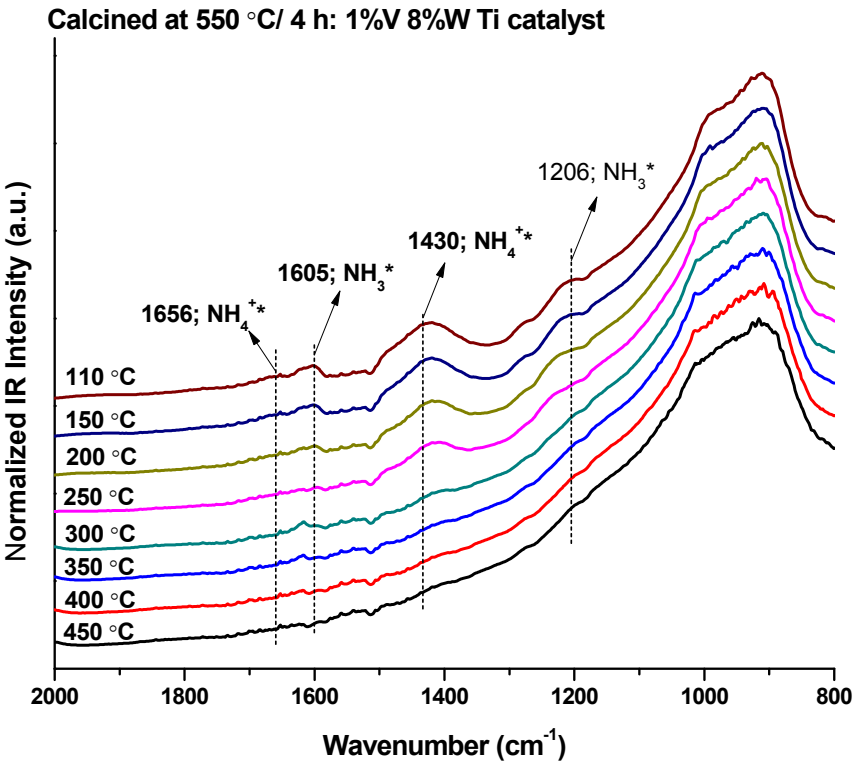
E) 650°C Calcined: 1%V_2O_5 – 5%WO_3/TiO_2



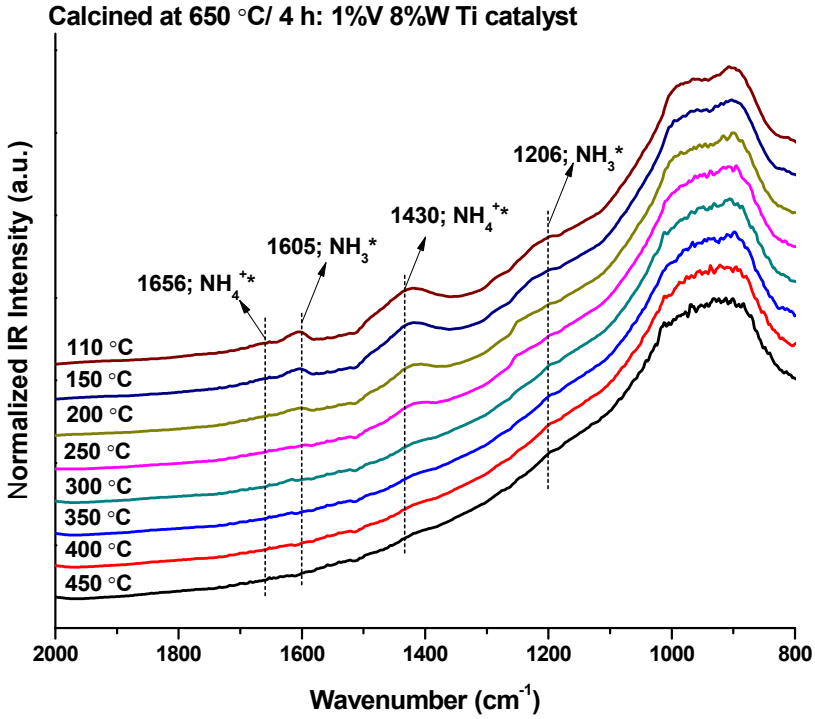
F) 650°C Hydrothermally aged: 50 hr 1%V_2O_5 – 5%WO_3/TiO_2



G) 550°C Calcined: 1%V_2O_5 – 8%WO_3/TiO_2



H) 650°C Calcined: 1%V_2O_5 – 8%WO_3/TiO_2



I) 650°C Hydrothermally aged: 50 hr 1%V_2O_5 – 8%WO_3/TiO_2

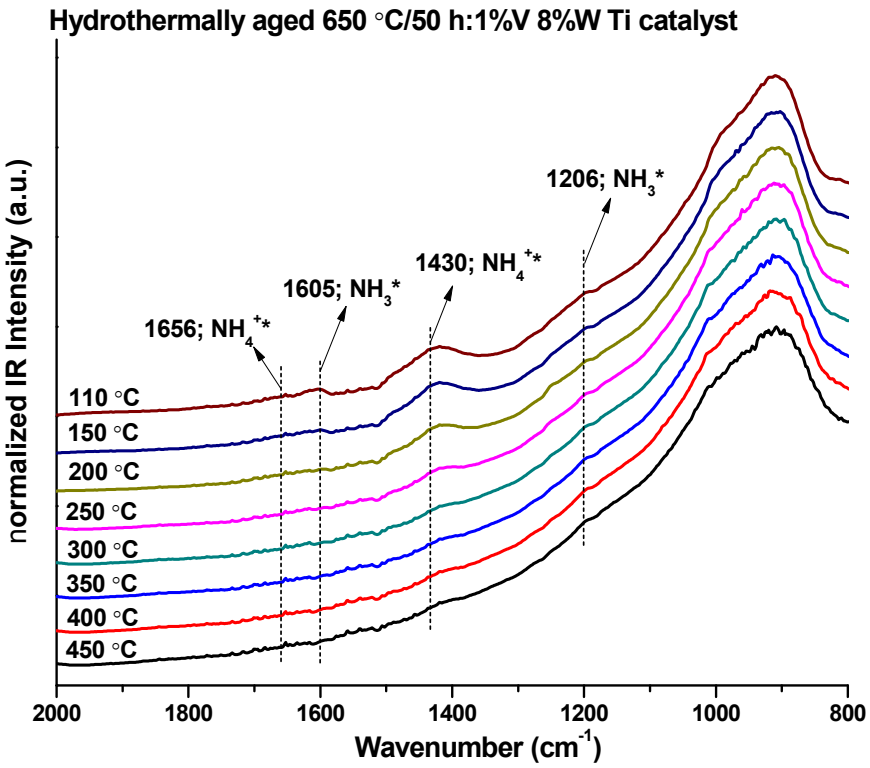


Figure S3. *In situ* TP-IR spectra of surface NH_3* (1206 cm^{-1}) and NH_4^+* (1425 cm^{-1}) species on titania-supported V_2O_5-WO_3 catalysts after calcination at 550°C and 650°C, and hydrothermal treatment at 650°C, spectra taking during SCR of adsorbed ammonia in flowing NO/O_2. The intensities of the IR bands from the surface ammonia species are normalized with respect to the strong TiO_2 IR band at ~940 cm^{-1}.

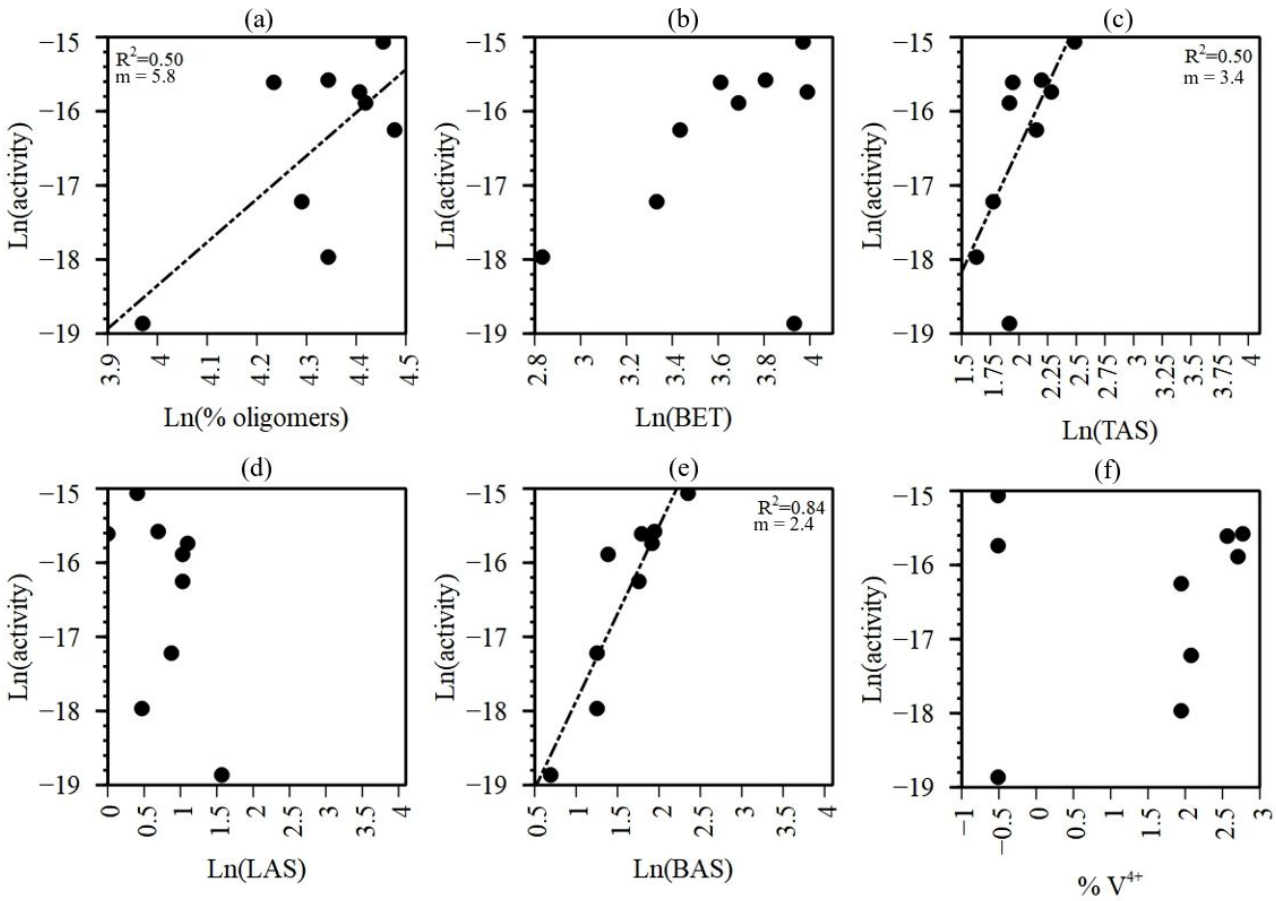


Figure S4. Log-log Correlation plots between steady-state SCR TOF values at 200°C and structural properties of the series of supported VWTi catalysts: (a) surface VO_x oligomer sites (%), (b) BET (m^2/g), (c) total number of adsorbed ammonia species, (d) number of surface NH_3* species, (e) number of surface NH_4^+* species, and (f) V^{4+} sites (%). Slopes and correlation coefficients for (a) surface VO_x oligomer sites (%), (c) total number of adsorbed ammonia species, and (e) number of surface NH_4^+* species are shown.

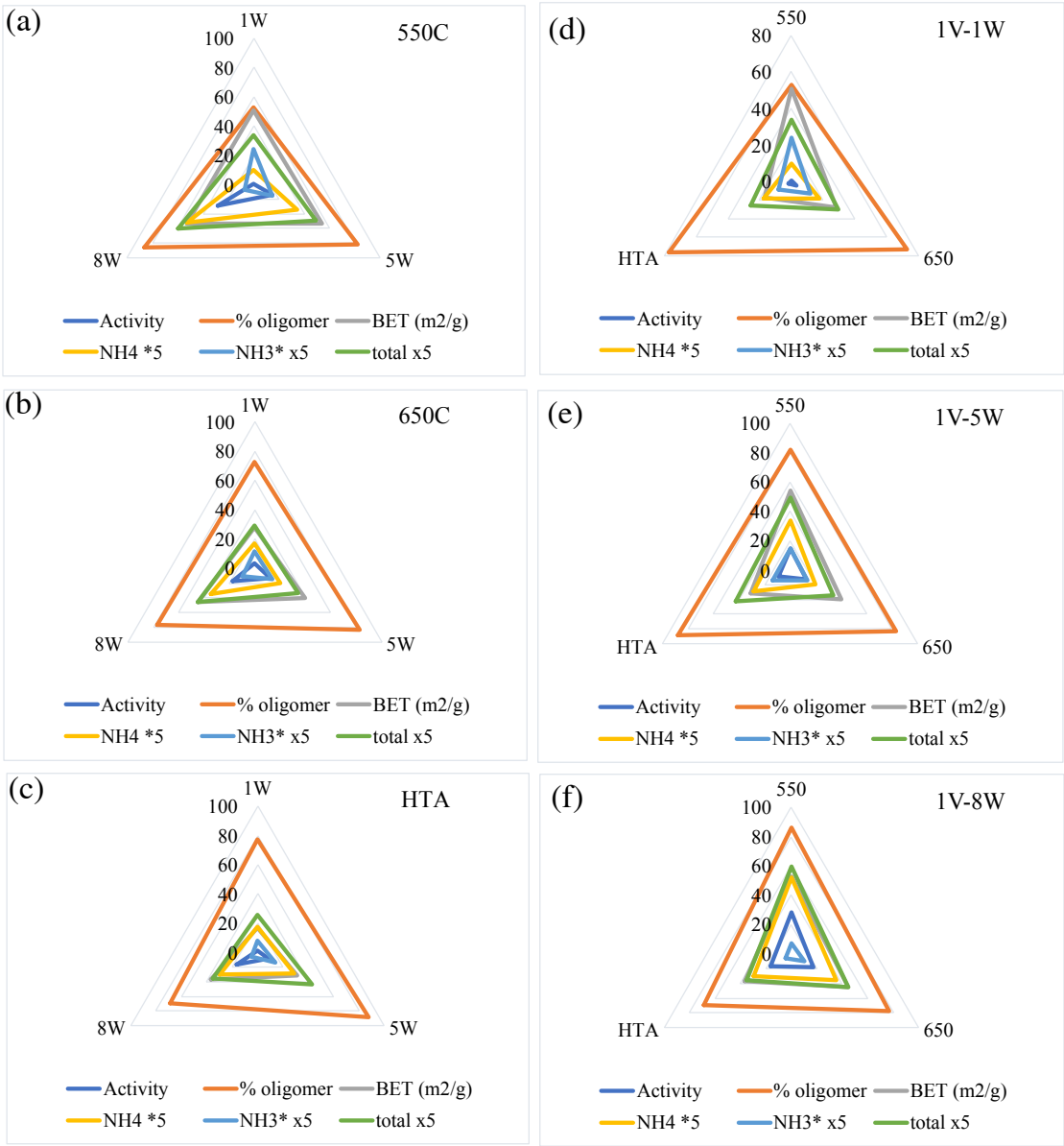


Figure S5. Radar plot of catalytic activity and catalyst properties (number of Lewis acid sites (NH_3*), number of Brønsted acid sites (NH_4^+*), total number of acid sites (Lewis and Brønsted), BET surface area, and fraction of surface vanadia oligomers, as a function of thermal treatment (a-c) and as a function of W loading (d-f).

References

1. Kompio, P. G.; Brückner, A.; Hipler, F.; Auer, G.; Löffler, E.; Grünert, W., A New View on the Relations between Tungsten and Vanadium in V2O5WO3/TiO2 Catalysts for the Selective Reduction of NO with Nh3. *Journal of Catalysis* **2012**, *286*, 237-247.
2. Kompio, P. G. W. A., Der Einfluss Von Hochtemperaturbehandlungen Auf\(V_ {2} O_ {5}-WO_ {3}/TiO_ {2}\)-Katalysatoren Für Die Selektive Katalytische Reduktion Von Stickoxiden Mit Ammoniak. **2010**.
3. Paganini, M. C.; Dall'Acqua, L.; Giamello, E.; Lietti, L.; Forzatti, P.; Busca, G., An Epr Study of the Surface Chemistry of the V2O5–WO3/TiO2 catalyst: Redox Behaviour and State of V (Iv). *Journal of Catalysis* **1997**, *166*, 195-205.
4. Chang, T.-T., Paramagnetic-Resonance Spectrum of W 5+ in Rutile (Ti O 2). *Physical Review* **1966**, *147*, 264.

5. Bravo, D.; Ruiz, X.; Diaz, F.; López, F., Epr of Tungsten Impurities in Ktiopo 4 Single Crystals Grown from Molten Tungstate Solutions. *Physical Review B* **1995**, *52*, 3159.
6. Schirmer, O.; Salje, E., The W5+ Polaron in Crystalline Low Temperature WO3 Esr and Optical Absorption. *Solid State Communications* **1980**, *33*, 333-336.