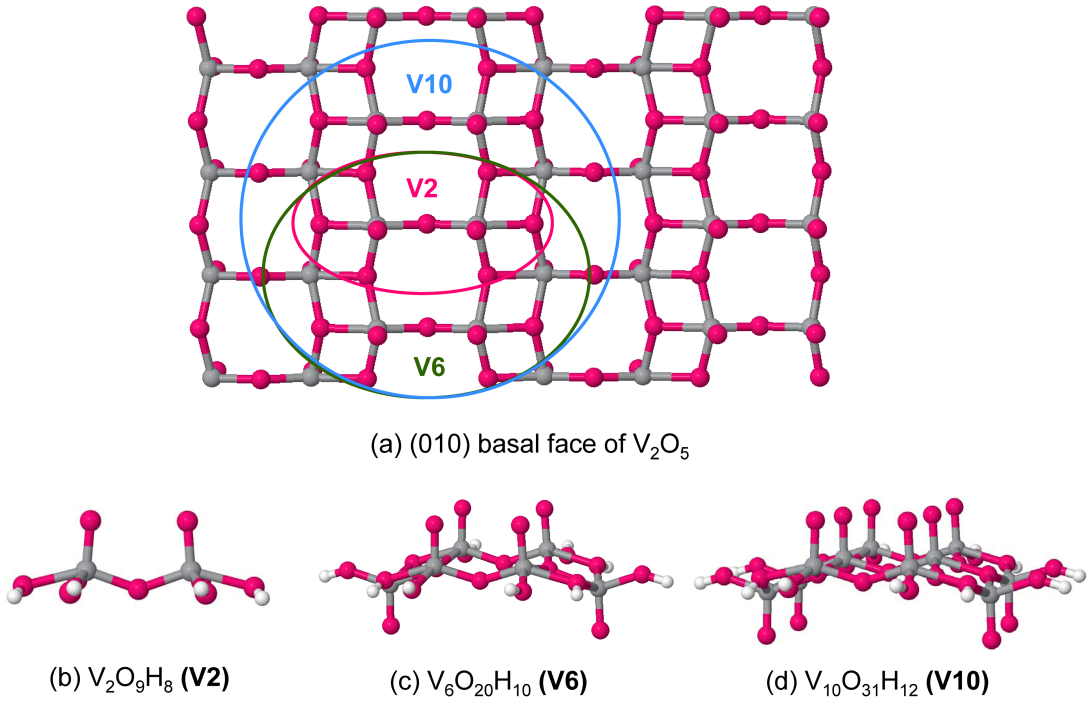

Fig. 1S Structures of cluster models used to represent the (010) surface of V_2O_5.

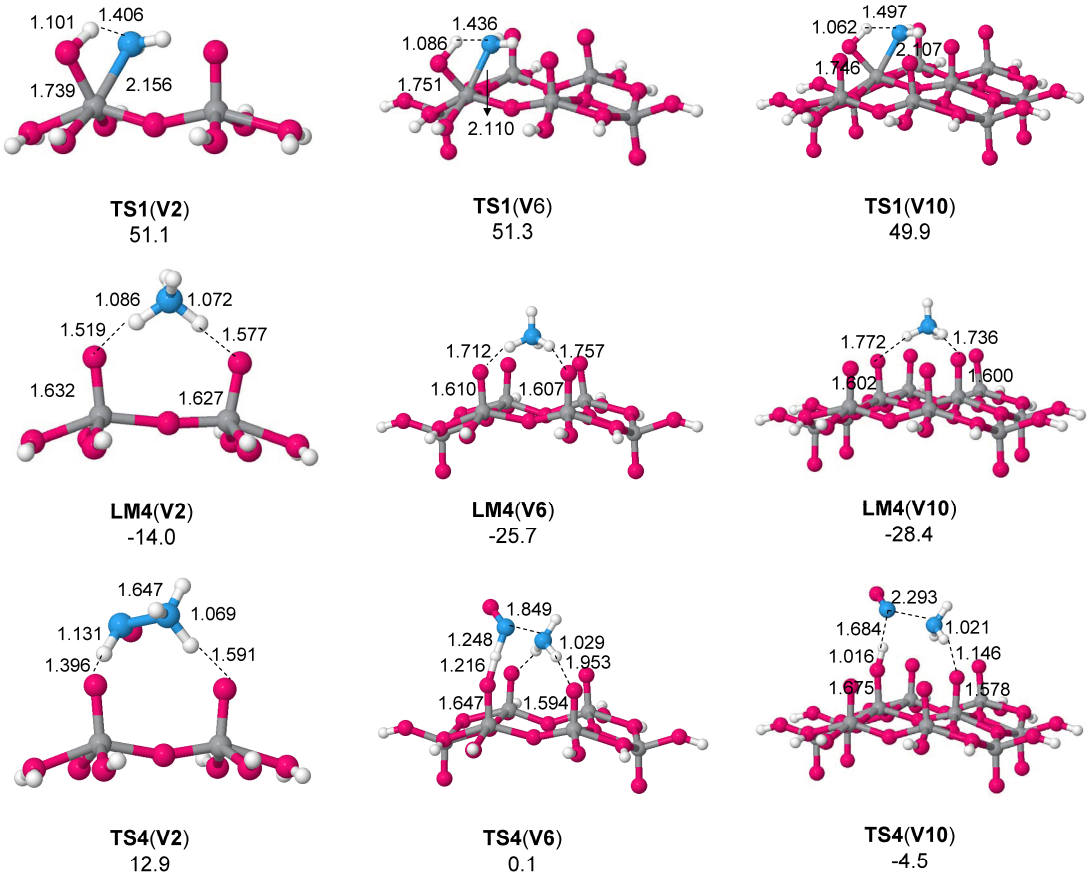

Fig. 2S Optimized geometries and energetics of selected LMs and TS' (bond length in Å; relative energy in kcal mol^{-1}).

Table 1S. Theoretical benchmark for test reactions.

Reactions	ΔH_{298}(kcal mol^{-1})	
	Calc.	Expt.
$NO \rightarrow 0.5N_2 + 0.5O_2$	21.7	21.8[a]
$NH_3 \rightarrow 0.5N_2 + 1.5H_2$	-13.0	-11.0[a]
$NH_3 \rightarrow NH_2 + H$	105.0	107.6[b]
$NH_3 + H^+ \rightarrow NH_4^+$	-201.7	-204.0[b]
$NH_3 \rightarrow NH_3^+ + e$	235.0	232.2[c]
$NH_4^+ \rightarrow NH_3^+ + H$	123.0	122.5[d]

a. *CRC Handbook of Chemistry and Physics, 82nd ed.*; CRC Press: Boca Raton, Fl, 2002.

b. Y. Luo, *Comprehensive handbook of chemical bond energies.* CRC Press: Boca Raton, Fl, 2007.

c. Data from http://webbook.nist.gov/chemistry/

d. Data deduced from ref. b and ref. c