Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for "A theoretical study of the effect of a non-aqueous proton donor on electrochemical ammonia synthesis"

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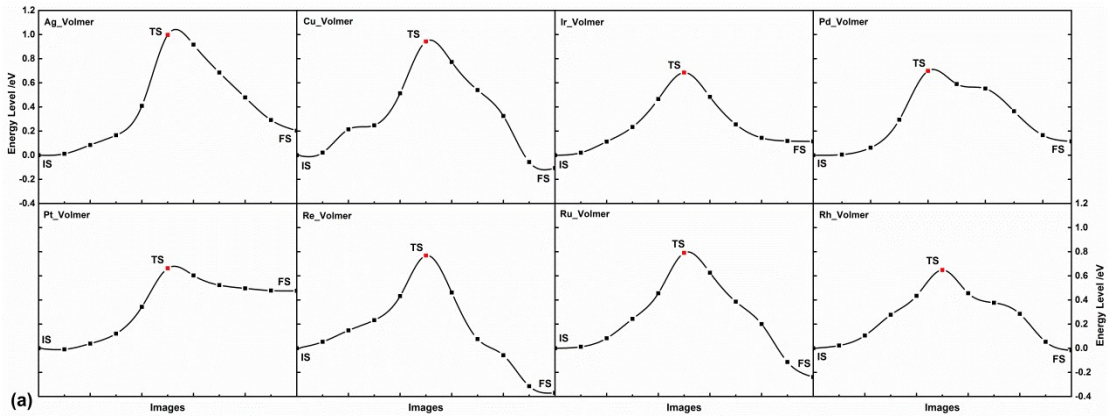
Table S1 The optimized lattice constant a (in Å) for each metal studied in this work.

	Ag(111)	Cu(111)	Ir(111)	Pd(111)	Pt(111)	Re(111)	Rh(111)	Ru(111)
a /Å	4.21	3.69	3.88	3.97	4.00	3.89	3.85	3.85

Table S2 Free energy corrections (ZPE - TS) of gas phase molecules and adsorbed intermediates at 300 K and 101325 Pa (in eV).

	H_2	**N_2**	**NH_3**			
ZPE-TS	-0.02	-0.35	0.44			
ZPE-TS	***N_2**	***NNH**	***NNH_2**	***N**	***NH**	***NH_2**
@Ag(111)	-0.09	0.33	--	0.05	0.34	0.63
@Cu(111)	-0.09	0.40	--	0.07	0.36	0.66
@Ir(111)	0.14	0.46	--	0.08	0.38	0.71
@Pd(111)	0.06	0.40	--	0.08	0.37	0.67
@Pt(111)	0.11	0.45	--	0.08	0.39	0.71
@Re(111)	0.13	0.48	0.77	0.09	0.39	0.70
@Rh(111)	0.08	0.38	--	0.08	0.37	0.68
@Ru(111)	0.12	0.41	0.77	0.09	0.38	0.68

Figure S1 Calculated NEB profiles using $LutH^+$ as proton donor for Volmer-(a) and Heyrovsky-(b) reaction on different transition metal facets, respectively. All the transition states (TS) have been verified using vibrational analyses and are highlighted in red in the plots. The barrier is taken as the energy difference between this transition state and the initial state (IS). Owing to the difficulties in locating the transition state for the Heyrovsky reaction on Rh(111), there is no data reported for Rh here in plot (b) and in Figure 4b in the main text.



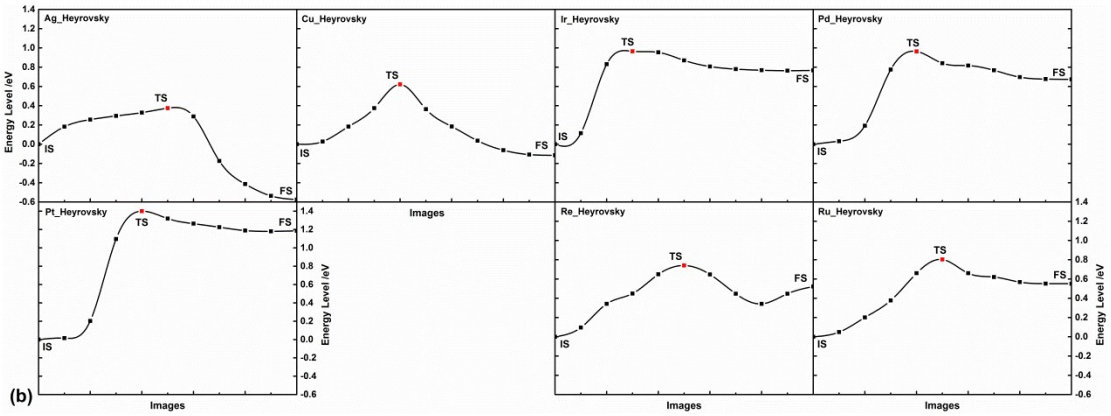


Figure S2 Projected density of states (PDOS) on H (in transition state TS) transferred from H_3O^+ and also the O atoms in the water molecule. The Fermi level corresponds to the origin of the energy-axis.

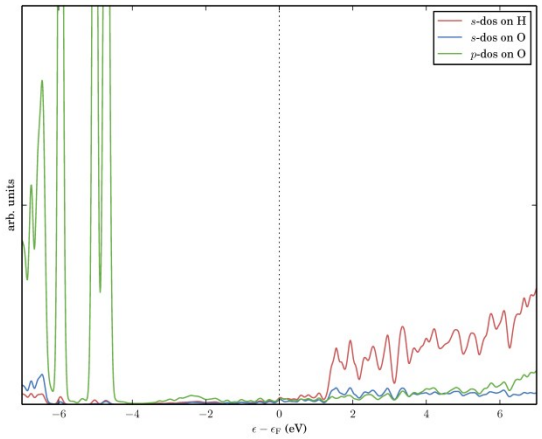


Figure S3 Free energy diagram for the associative reduction of N_2 on Re(111) (black). The using of $LutH^+$ has been shown in red. Results are obtained from DFT calculations of the binding energies and vibrational frequencies, as well as entropy of the gas molecules. An asterisk, *, denotes an adsorption site on the surface.