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Decomposition Pathways of Formamide in the Presence of Vanadium and Titanium Monoxides

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Table S1. Theoretically reported energy barriers (kcal/mol) of the two-step dehydrations of FM without and with water and FM as catalysts in the S_0, S_1 and T_1 states. (Adapted from ref [1])

Reference systems	Energy barriers[(a)] (kcal/mol)		
	Step 1: Isomerization	Step 2: Dehydration	Overall
FM (S_0)[2]	43.9	59.1	73.6
FM (S_0)[3]	48.9		
FM (S_0)[4]	44.7		
FM (S_1)[5]	35.8	75.8	78.3
FM (T_1)[5]	19.1	56.7	50.5
FM...H_2O (S_0)[3]	22.6		
FM...H_2O (S_0)[4]		33.5	
FM...H_2O (S_0)[6]	20.0	37.8	49.4
FM...$2H_2O$ (S_0)[6]	17.2	32.9	38.0
			54.2[(b)]
FM...$3H_2O$ (S_0)[6]	20.9	33.5	31.3
			53.8[(b)]
FM...FM (S_0)[7]	26.1	18.7	48.1
FM (on pyrite surface)[1]	44.6		
FM...H_2O (on defect pyrite surface) [1]	14.4		
FM...OH groups (of kaolinite surface)[8]	18.0		
FM...H_2O...OH groups (of kaolinite surface)[8]	19.8		

[(a)] The energy barriers for step 1 and 2 are scaled with respect to the reactants directly involved in each elementary step, whereas the *overall* energy barriers are scaled with respect to the sum of the energies of separated reactants.

[(b)] These values are scaled with respected to the complexes between FM and waters.

Table S2. Charge distribution of the complexes between VO/TiO and FM obtained from NBO analysis.

	1a	**1a$^{(TiO)}$**	**1b**	**1b$^{(TiO)}$**
V/Ti	1.07902	1.15570	1.55760	1.52699
$O^{(VO/TiO)}$	-1.15017	-1.22555	-1.25977	-1.24302
N	-0.83178	-0.82371	-0.77157	-0.76639
C	0.71401	0.72221	0.56795	0.56506
$O^{(FM)}$	-0.83948	-0.86582	-1.02896	-1.02259

Table S3. Selected bond lengths of the complexes between VO/TiO and FM obtained from BP86 calculations.

	1a	**1a$^{(TiO)}$**	**1b**	**1b$^{(TiO)}$**
$V/Ti{-}O^{(VO/TiO)}$	1.645	1.666	1.771	1.811
C−N	1.331	1.333	1.275	1.277
$C{-}O^{(FM)}$	1.271	1.276	1.337	1.337
$V/Ti{-}O^{(FM)}$	1.995	2.003	1.810	1.858
$O^{(VO/TiO)}{-}H^{(FM)}$	1.803	1.782		

References

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