Pyruvic acid, an efficient catalyst in SO_3 hydrolysis and an effective clustering agent in sulfuric acid-based new particle formation

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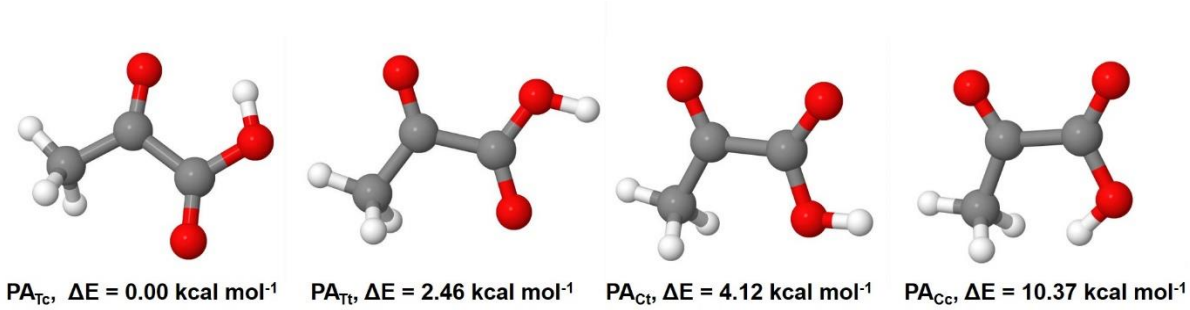

Figure S1: Conformers of PA optimized with the M06-2X/6-311++G(3df,3pd) method. Energies values, calculated at the M06-2X/6-311++G(3df,3pd) level of theory, are given relative to the energy of PA$_{Tc}$.

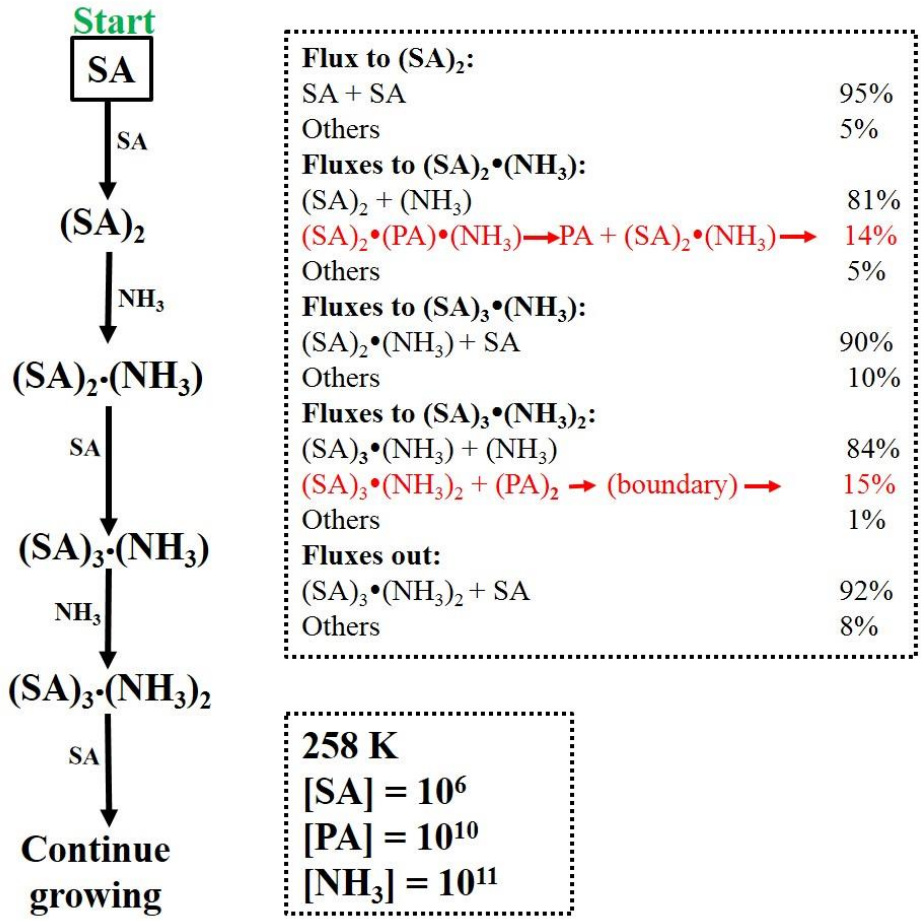

Figure S2: Main cluster pathways at 258 K, [SA] = 10^6 cm^{-3}, [PA] = 10^{10} cm^{-3}, and [NH_3] = 10^{11} cm^{-3}. Red color indicates the path involving PA.

Table S1: Electronic (ΔE) and Gibbs free energies at 298 K and 1 atm (ΔG) of formation of all intermediate in H2O-ctalayzed and PA-catalyzed SO3 hydrolysis. Corresponding structures are shown in **Figure 1** and **Figure 2** in the main article. Energies units are kcal mo^{l-1}.

	Without ZPE correction		With ZPE correction	
Clusters	ΔE	ΔG	ΔE	ΔG
$H_2O \cdot H_2O$	-5.00	2.62	-2.90	4.72
$SO_3 \cdot H_2O$	-9.00	1.02	-6.67	3.35
$PA_{Tt} \cdot H_2O$	-10.26	0.51	-8.03	2.75
$PA_{Ct} \cdot H_2O$	-10.90	0.02	-8.64	2.29
Water-catalyzed reaction				
RC	-20.91	1.78	-15.40	7.30
TS	-13.72	8.36	-9.93	12.15
PC	-34.98	-11.51	-29.25	-5.78
PA-catalyzed reaction				
RC_{Tt}	-24.59	-0.41	-20.60	3.59
TS_{Tt}	-22.01	0.91	-20.25	2.67
PC_{Tt}	-39.13	-14.87	-34.81	-10.55
RC_{Ct}	-26.11	-1.47	-22.15	2.49
TS_{Ct}	-24.01	-0.60	-24.01	1.34
PC_{Ct}	-41.16	-16.49	-34.73	-12.05

Table S2: Electronic and Gibbs free energies of clusters formation in the sulfuric acid-pyruvic acid-ammonia system. Energies units are kcal mo^{l-1}.

Clusters	**$\triangle E_{0K}$**	**$\triangle G_{298K}$**	**$\triangle G_{278K}$**	**$\triangle G_{258K}$**	**$\triangle G_{238K}$**
$(PA)_2$	-15.40	-3.57	-4.30	-5.03	-5.76
$(PA)_3$	-25.38	-1.32	-2.79	-4.26	-5.73
$(PA)_1 \bullet (NH_3)_1$	-11.60	-2.47	-3.00	-3.53	-4.06
$(PA)_2 \bullet (NH_3)_1$	-24.17	-3.79	-5.00	-6.21	-7.42
$(PA)_2 \bullet (NH_3)_2$	-37.04	-3.02	-5.08	-7.13	-9.18
$(PA)_3 \bullet (NH_3)_1$	-42.41	-3.36	-5.75	-8.14	-10.53
$(PA)_3 \bullet (NH_3)_2$	-58.56	-6.08	-9.19	-12.31	-15.42
$(PA)_3 \bullet (NH_3)_3$	-68.39	-7.27	-10.89	-14.50	-18.11
$(PA)_1 \bullet (SA)_1$	-18.46	-6.18	-6.94	-7.70	-8.47
$(PA)_1 \bullet (SA)_2$	-39.05	-12.75	-14.37	-15.99	-17.61
$(PA)_1 \bullet (SA)_3$	-57.28	-15.87	-18.42	-20.98	-23.53
$(PA)_2 \bullet (SA)_1$	-35.49	-11.93	-13.39	-14.85	-16.31
$(PA)_2 \bullet (SA)_2$	-51.12	-13.84	-16.13	-18.42	-20.72
$(PA)_2 \bullet (SA)_3$	-70.31	-17.16	-20.41	-23.66	-26.91
$(PA)_1 \bullet (SA)_1 \bullet (NH_3)_1$	-32.16	-9.80	-11.16	-12.52	-13.89
$(PA)_1 \bullet (SA)_1 \bullet (NH_3)_2$	-53.85	-15.54	-17.77	-20.00	-22.23
$(PA)_2 \bullet (SA)_1 \bullet (NH_3)_1$	-53.25	-15.42	-17.68	-19.95	-22.21
$(PA)_2 \bullet (SA)_1 \bullet (NH_3)_2$	-71.95	-22.47	-25.45	-28.42	-31.40

$(PA)_2$•$(SA)_1$•$(NH_3)_3$	-83.24	-22.10	-25.75	-29.40	-33.05
$(PA)_1$•$(SA)_2$•$(NH_3)_1$	-62.19	-24.58	-26.84	-29.10	-31.36
$(PA)_1$•$(SA)_2$•$(NH_3)_2$	-87.35	-32.66	-35.86	-39.05	-42.25
$(PA)_1$•$(SA)_2$•$(NH_3)_3$	-99.35	-35.03	-38.84	-42.64	-46.44
$(SA)_2$	-21.63	-7.34	-8.20	-9.07	-9.93
$(SA)_3$	-41.03	-12.94	-14.67	-16.41	-18.14
$(SA)_1$•$(NH_3)_1$	-17.40	-6.67	-7.31	-7.95	-8.59
$(SA)_2$•$(NH_3)_1$	-47.44	-21.61	-23.13	-24.65	-26.17
$(SA)_2$•$(NH_3)_2$	-66.86	-27.60	-29.84	-32.07	-34.31
$(SA)_3$•$(NH_3)_1$	-69.61	-30.15	-32.53	-34.91	-37.28
$(SA)_3$•$(NH_3)_2$	-96.16	-43.42	-46.46	-49.50	-52.54
$(SA)_3$•$(NH_3)_3$	-112.42	-47.83	-51.57	-55.32	-59.06