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Electronic Supplementary Information

Effect of fluorine substitution on structures and reactivity of Keggin-Al_{13} in aqueous solution: An exploration of the fluorine substitution mechanism.

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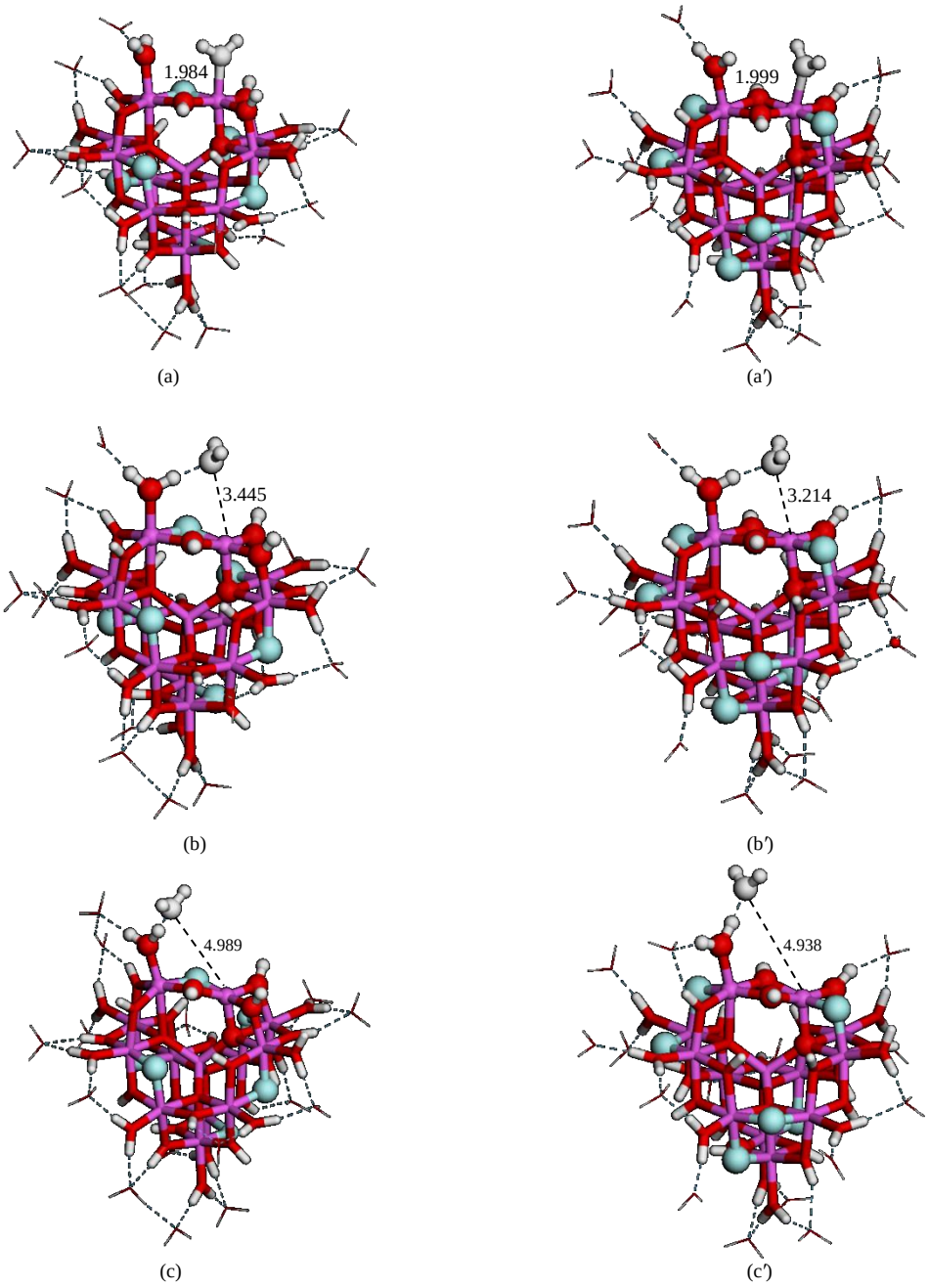


Fig. S1 The water exchange pathways of fluoridated K-Al_{13}-6F. (a), (b) and (c) denote the optimized reactant, transition state and intermediate for K-Al_{13}-6F with inter-trimer bridging fluoridated sites, respectively. (a′), (b′) and (c′) denote the optimized reactant, transition state and intermediate for K-Al_{13} with intra-trimer bridging fluoridated sites, respectively. The target water molecule is colored with white.

Table S1. Energy barriers (kJ·mol^{-1}) of water exchange on K-Al_{13}-1F and K-Al_{13}-6F relative to reactant.

	K-Al_{13}-1F		K-Al_{13}-6F	
	μ_2-F(1)	μ_2-F(2)	μ_2-F(1)	μ_2-F(2)
TS	44.5	38.2	44.1	39.1
P	39.6	35.1	40.1	36.8

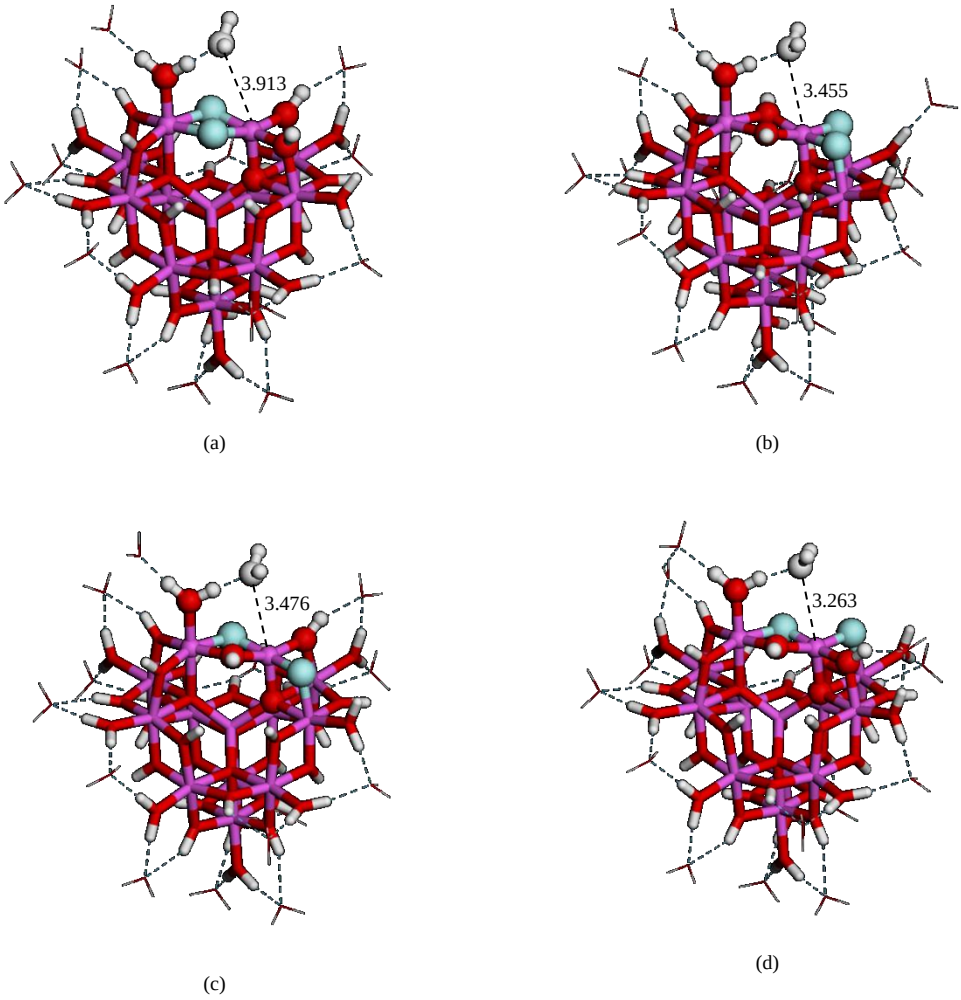
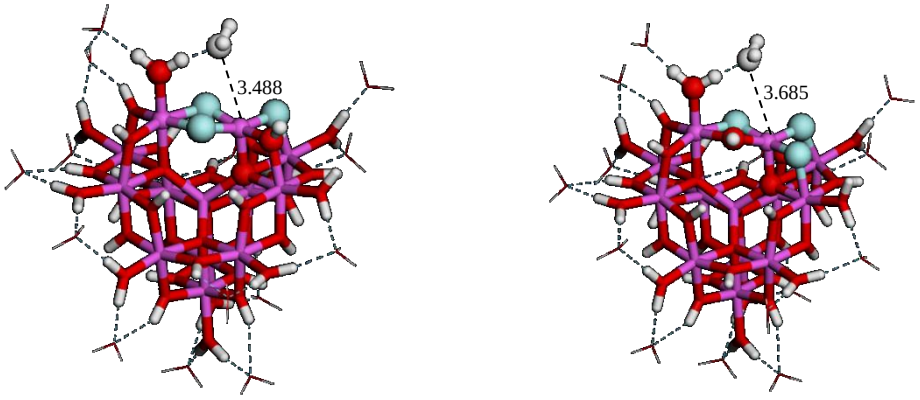


Fig. S2 The transition state of water exchange on fluoridated K-Al_{13}-2F. (a) two inter-trimer hydroxyl bridges are substituted by F^-; (b) two intra-trimer hydroxyl bridges are substituted by F^-; (c) one inter-trimer and one intra-trimer hydroxyl bridges are cis-substituted; (d) one inter-trimer and one intra-trimer hydroxyl bridges are trans-substituted. The target water molecule is colored with white.

Table S2. Structural change in the water-exchange activated process of K-Al_{13}-2F.

Distances	(a)		(b)		(c)		(d)	
（Å）	R	TS	R	TS	R	TS	R	TS
Al-O_L	1.965	3.913	1.979	3.455	1.994	3.476	1.982	3.263
Al-O_t	1.961	1.859	1.994	1.876	1.988	1.871	1.995	1.882
Al-F_1	1.915	1.854	1.880	1.856	1.889	1.880	1.881	1.859
Al-F_2	1.906	1.852	1.874	1.849	1.867	1.859	1.890	1.854
Al-O_1	1.838	1.821	1.856	1.816	1.872	1.813	1.867	1.828
Al-O_2	1.858	1.846	1.847	1.820	1.840	1.813	1.846	1.816
∑Al-L	11.443	13.145	11.370	12.672	11.450	12.712	11.461	12.502
Δ∑Al-L	1.701		1.301		1.262		1.041	
Al_t-O	1.908	1.900	1.909	1.900	1.907	1.900	1.908	1.901



(a) (b)

Fig. S3 The transition state of water exchange on fluoridated K-Al_{13}-3F. (a) two inter-trimer and one intra-trimer hydroxyl bridges are substituted by F^-; (b) one inter-trimer and two intra-trimer hydroxyl bridges are substituted by F^-. The target water molecule is colored with white.

Table S3. Structural change in the water-exchange activated process of K-Al_{13}-3F.

Distances	(a)		(b)	
（Å）	R	TS	R	TS
Al-O_L	1.980	3.488	1.980	3.685
Al-O_t	1.933	1.841	1.940	1.827
Al-F_1	1.877	1.830	1.858	1.842
Al-F_2	1.862	1.839	1.859	1.830
Al-F_3	1.881	1.843	1.872	1.853
Al-O_1	1.846	1.823	1.850	1.803
∑Al-L	11.379	12.664	11.359	12.840
Δ∑Al-L	1.285		1.481	
Al_t-O	1.903	1.894	1.904	1.888

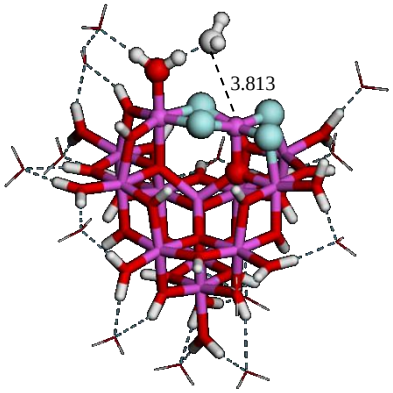


Fig. S4 The transition state of water exchange on fluoridated K-Al_{13}-4F.

Table S4. Structural change in the water-exchange activated process of K-Al_{13}-4F.

Distances（Å）	R	TS
Al-O_L	1.960	3.813
Al-O_t	1.911	1.816
Al-F_1	1.848	1.819
Al-F_2	1.868	1.829
Al-F_3	1.849	1.826
Al-F_4	1.854	1.827
∑Al-L	11.290	12.930
Δ∑Al-L	1.640	
Al_t-O	1.903	1.885

Table S5. Energy barriers (kJ·mol^{-1}) of water exchange on K-Al_{13}-nF (n=1~4) relative to reactant.

Barriers	A	B	C	D
K-Al_{13}-0F	28.7	-	-	-
K-Al_{13}-1F	44.5	38.2	-	-
K-Al_{13}-2F	45.1	48.9	40.8	51.2
K-Al_{13}-3F	65.1	61.9	-	-
K-Al_{13}-4F	79.5	-	-	-

Table S6. The influence of fluoridation on NPA charges (e) on octahedral Al of monomer aluminum and K-Al_{13}.

Charges	K-Al_{13}-0F	K-Al_{13}-6F		$Al(H_2O)_5(OH)$	$Al(H_2O)_5F$
		μ_2-F(1)	μ_2-F(2)		
Al	2.050	2.046	2.044	1.945	1.970