Experimental Study on the Dissociation Equilibrium of (CH_4+CO_2+N_2) Hydrates in the Mixed Sediments

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The particle diameter was measured with the Mastersizer 2000 particle size analyzer. Around 0.5 g sample was put into a glass breaker, adding 1000 mL water and 20 mL sodium hexametaphosphate (0.5 mol·L^{-1}) as dispersant. The mixture was stirred 1 min then used for the particle size distribution test, and the measurement of particle size range is from 0.02 μm to 2000 μm. The specific surface area, pore diameter and pore volume were determined based on the N_2 adsorption-desorption analysis, which was carried out on a Micromeritics ASAP 2010 instrument. About 0.2 g sample in a tube was pretreated at 300 ℃ for 4 h under vacuum firstly, the treated sample was performed at −196 ℃ in the liquid nitrogen. The surface area of the sample was obtained using the Brunauer-Emmett-Teller (BET) equation,[1] the total pore volume was calculated from the desorption branch of the isotherm at P/P_0=0.995 to assume complete pore saturation, the average pore diameter was calculated on the basic of the pore volume and surface area.

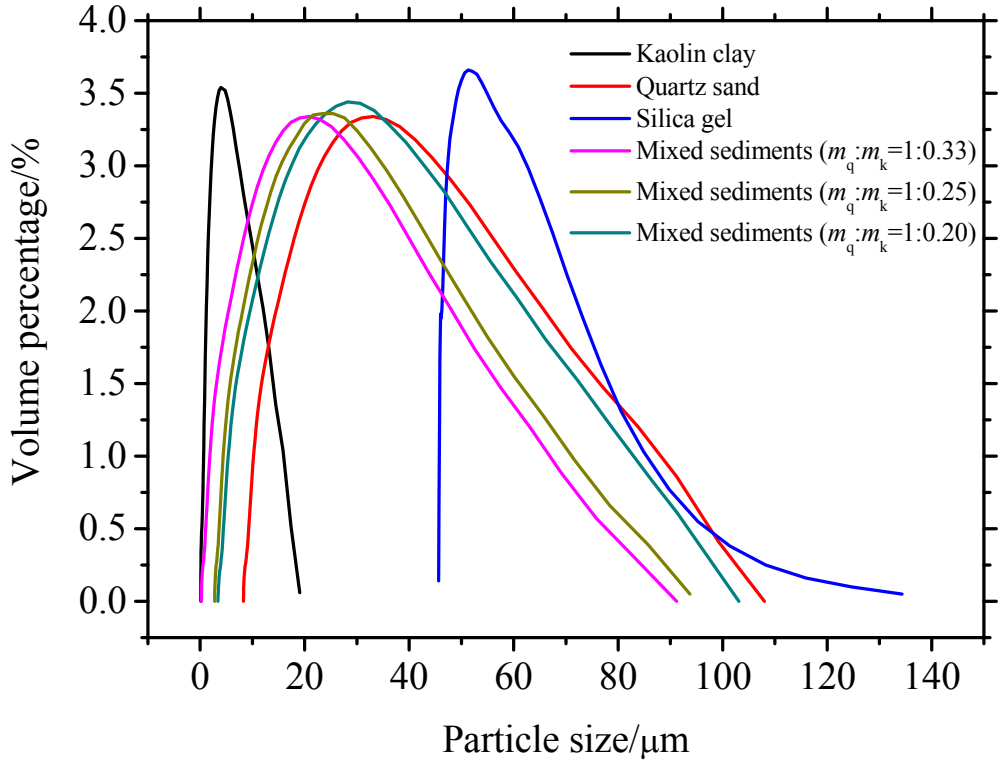
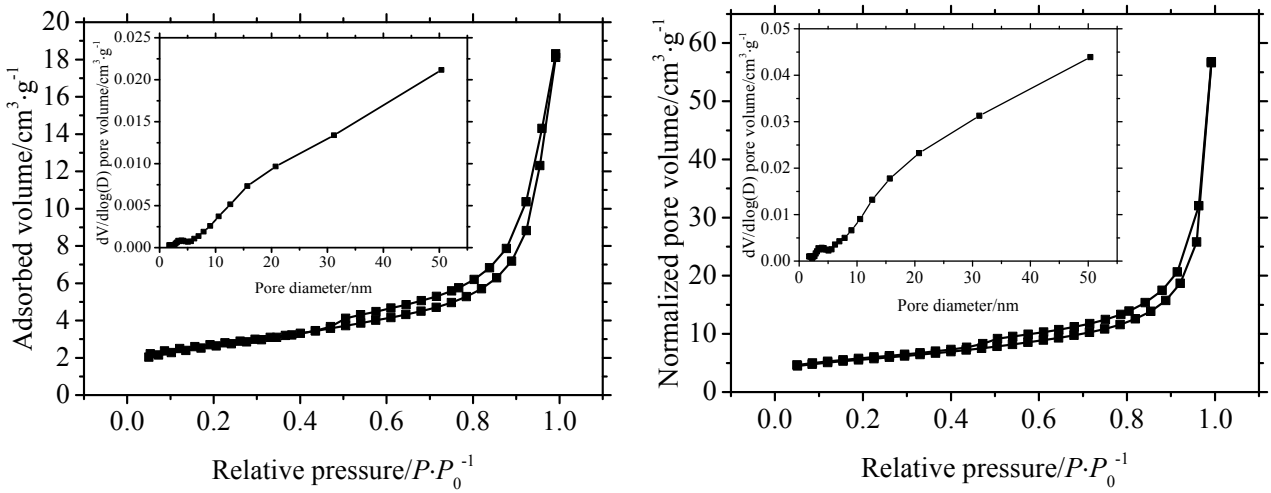


Figure S1. The particle size distribution of materials used in this work.



(a) (b)

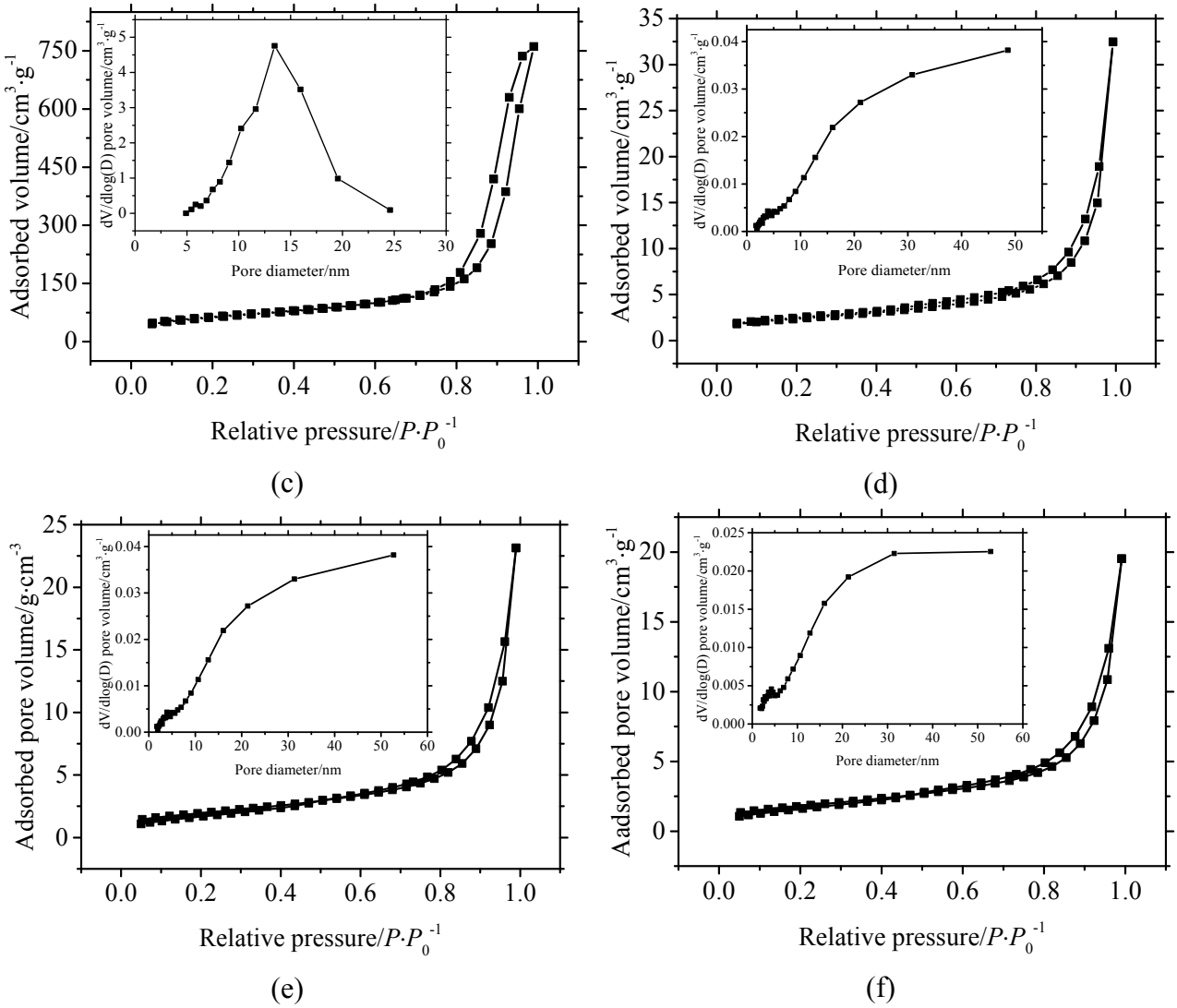


Figure S2. N_2 adsorption-desorption and pore size distribution of materials: (a) quartz sand, (b) kaolin clay, (c) silica gel, (d) m_q:m_k=1:0.33, (e) m_q:m_k=1:0.25, (f) m_q:m_k=1:0.20.

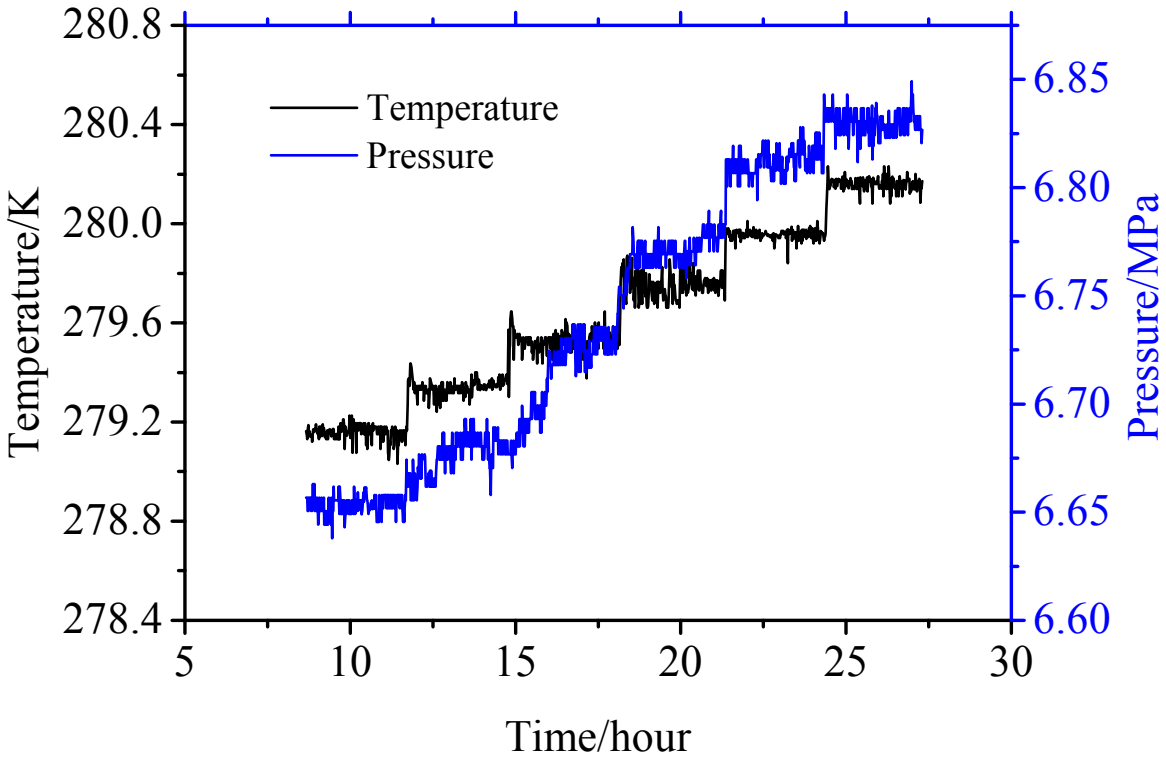


Figure S3. The pressure and temperature *vs.* time curves during the stepwise heating process in one test.

Table S1. The Calculation of the Hydrate Dissociation Enthalpies[a,b]

Gas	m_q:m_k	S_w	$10^3/T$/K^{-1}	lnP/MPa	y_1/ mol%	y_2/ mol%	y_3/ mol%	z	k	ΔH/kJ·mol^{-1}
M_1	1:0.20	30%	3.659	1.606	15.03	20.28	64.69	0.9235	-9530.41	73.17
			3.645	1.714	15.02	20.33	64.65	0.9176	-9530.41	72.71
			3.632	1.827	15.01	20.37	64.62	0.9113	-9530.41	72.21
			3.621	1.943	15.00	20.41	64.59	0.9046	-9530.41	71.68
			3.608	2.081	14.99	20.45	64.56	0.8971	-9530.41	71.08
			3.600	2.162	14.99	20.47	64.55	0.8932	-9530.41	70.77
M_2	1:0.20	30%	3.658	1.445	40.66	14.17	45.17	0.9234	-8784.91	67.44
			3.641	1.582	40.64	14.21	45.15	0.9151	-8784.91	66.84
			3.622	1.744	40.61	14.26	45.13	0.9046	-8784.91	66.07
			3.607	1.885	40.59	14.30	45.12	0.8949	-8784.91	65.36
			3.592	2.020	40.57	14.33	45.10	0.8858	-8784.91	64.70
			3.581	2.120	40.55	14.35	45.10	0.8796	-8784.91	64.24
M_2	1:0.33	30%	3.656	1.536	40.50	14.51	44.99	0.9165	-8550.48	65.15
			3.641	1.652	40.50	14.51	45.00	0.9091	-8550.48	64.63
			3.623	1.792	40.49	14.51	45.00	0.9000	-8550.48	63.98
			3.608	1.923	40.49	14.51	45.01	0.8910	-8550.48	63.34
			3.596	2.039	40.48	14.51	45.01	0.8832	-8550.48	62.79
			3.585	2.145	40.48	14.51	45.01	0.8764	-8550.48	62.30
M_2	1:0.25	30%	3.659	1.477	40.66	14.17	45.17	0.9213	-8652.47	66.28
			3.642	1.603	40.64	14.21	45.15	0.9136	-8652.47	65.72
			3.627	1.733	40.61	14.25	45.14	0.9051	-8652.47	65.11

			3.614	1.846	40.60	14.28	45.12	0.8974	-8652.47	64.56
			3.599	1.986	40.57	14.32	45.11	0.8879	-8652.47	63.87
			3.587	2.097	40.56	14.34	45.10	0.8808	-8652.47	63.36
M_3	1:0.20	30%	3.656	1.292	84.68	3.66	11.67	0.9176	-7860.25	59.97
			3.638	1.413	84.66	3.67	11.67	0.9092	-7860.25	59.42
			3.621	1.549	84.65	3.68	11.67	0.8987	-7860.25	58.73
			3.606	1.664	84.64	3.70	11.67	0.8892	-7860.25	58.11
			3.590	1.786	84.63	3.71	11.67	0.8786	-7860.25	57.42
			3.574	1.914	84.61	3.71	11.67	0.8672	-7860.25	56.67
			3.560	2.037	84.60	3.72	11.67	0.8561	-7860.25	55.95
			3.549	2.127	84.60	3.73	11.67	0.8482	-7860.25	55.43
M_4	1:0.20	30%	3.651	0.950	14.31	56.48	29.21	0.8983	-9573.44	71.50
			3.638	1.066	14.30	56.49	29.21	0.8866	-9573.44	70.57
			3.624	1.190	14.30	56.49	29.21	0.8727	-9573.44	69.46
			3.611	1.306	14.29	56.50	29.20	0.8580	-9573.44	68.29
			3.598	1.437	14.29	56.52	29.20	0.8388	-9573.44	66.76
			3.587	1.550	14.28	56.53	29.19	0.8205	-9573.44	65.31
			3.577	1.662	14.27	56.55	29.18	0.7996	-9573.44	63.64
M_5	1:0.20	30%	3.649	1.017	40.96	38.59	20.45	0.9075	-8790.85	66.33
			3.636	1.112	40.92	38.66	20.43	0.8992	-8790.85	65.72
			3.625	1.222	40.87	38.72	20.41	0.8883	-8790.85	64.92
			3.613	1.321	40.83	38.78	20.39	0.8778	-8790.85	64.16
			3.601	1.426	40.79	38.84	20.37	0.8655	-8790.85	63.26
			3.589	1.531	40.75	38.89	20.36	0.8516	-8790.85	62.24
			3.578	1.639	40.71	38.95	20.34	0.8366	-8790.85	61.14
M_5	1:0.20	20%	3.658	1.019	40.49	39.23	20.27	0.9055	-8213.02	61.83
			3.647	1.102	40.47	39.27	20.26	0.8981	-8213.02	61.33
			3.633	1.210	40.44	39.31	20.25	0.8876	-8213.02	60.61
			3.622	1.306	40.42	39.34	20.24	0.8773	-8213.02	59.90
			3.609	1.402	40.39	39.38	20.23	0.8664	-8213.02	59.16
			3.599	1.498	40.37	39.41	20.22	0.8541	-8213.02	58.32
			3.589	1.581	40.35	39.43	20.22	0.8428	-8213.02	57.55
			3.581	1.654	40.34	39.45	20.21	0.8322	-8213.02	56.83
M_5	1:0.20	40%	3.654	0.937	41.58	37.75	20.68	0.9154	-8897.02	67.71
			3.641	1.035	41.50	37.86	20.64	0.9076	-8897.02	67.14
			3.629	1.133	41.43	37.96	20.61	0.8989	-8897.02	66.49
			3.618	1.237	41.36	38.05	20.59	0.8887	-8897.02	65.74
			3.604	1.355	41.29	38.15	20.56	0.8759	-8897.02	64.79
			3.593	1.458	41.23	38.24	20.53	0.8635	-8897.02	63.87
			3.583	1.556	41.18	38.31	20.51	0.8507	-8897.02	62.93
			3.575	1.638	41.13	38.37	20.50	0.8390	-8897.02	62.06
M_6	1:0.20	30%	3.652	1.152	83.86	10.55	5.59	0.9163	-7825.51	59.62
			3.638	1.252	83.83	10.58	5.59	0.9089	-7825.51	59.13
			3.625	1.348	83.80	10.61	5.59	0.9011	-7825.51	58.63
			3.611	1.458	83.78	10.63	5.59	0.8914	-7825.51	58.00
			3.599	1.562	83.75	10.65	5.59	0.8815	-7825.51	57.35
			3.584	1.673	83.73	10.68	5.59	0.8703	-7825.51	56.62

[a] k is the slope, ΔH_a is the hydrate dissociation enthalpy, ΔH_b is the average hydrate dissociation enthalpy. y_1, y_2, y_3 are the concentration of CH_4, CO_2 and N_2 in the gas phase.

[b] Standard uncertainties u are $u(T)$ = 0.02 K, $u(P)$ = 0.025 MPa, $u(z)$ = 0.0001, $u(k)$ = 0.01, $u(\Delta H_a) = u(\Delta H_b)$ = 0.01 kJ·mol^{-1}. $u(y_1) = u(y_2) = u(y_2)$= 0.02 mol%

REFERENCES

(1) Brunauer, S.; Emmett, P.; Teller, E. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **1938**, *60*, 309–319.