

Supplementary Information

Direct probing of heterogeneity for adsorption and diffusion within SAPO-34 crystal

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Experimental Details

Sample preparation

SAPO-34 molecular sieves were synthesized as reported in literature.^{1,2} Detailed procedures were performed as follows.

Large crystal SAPO-34 was hydrothermally synthesized from the gel ratio of 1.0 morpholine (Mor): 1.0 Al₂O₃ : 1.0 P₂O₅ : 0.6 SiO₂ : 60 H₂O. The mixture of pseudo-boehmite (67.5 wt%), orthophosphoric acid (85 wt%) and deionized water were stirred for 1 h to form homogeneous aqueous. Then silica sol (30 wt%) and morpholine were added dropwise into the aqueous. The resulting gel was aged under vigorous stirring for 12 h at room temperature, then was transferred into stainless steel autoclave and heated at 200 °C for 48 h under rotation.

Nanosized SAPO-34 was synthesized from the gel ratio of 1.5 HEP : 1.0 Al₂O₃ : 1.0 P₂O₅ : 0.33 SiO₂ : 4.5TEA : 100 H₂O : 5% seed. 1-(2-hydroxy-ethyl)piperazine (HEP)-assisted synthesis of nanosized SAPO-34 was achieved with the use of a triethylamine (TEA) template and a small amount of ball-milled SAPO-34 seeds. Orthophosphoric acid and aluminium isopropoxide (99 wt%) were added into deionized water and stirred for 20 min. Subsequently, triethylamine (TEA, 99 wt%), tetraethyl orthosilicate (TEOS, 98 wt%), co-template (HEP) and the precursor were added in sequence. The amount of the precursor was calculated by the following formula: Precursor amount = 0.05 × M(Al₂O₃ + P₂O₅ + SiO₂)_{gel}, where precursor and M(Al₂O₃ + P₂O₅ + SiO₂)_{gel} stand for the weights of the ball-milled SAPO-34 and the dry mass of three inorganic oxides in the starting mixture, respectively. The mixture was stirred for 24 h. The resulting gel was transferred into stainless steel autoclave and heated at 200 °C for 24 h under rotation. After crystallization, all as-synthesized products were washed with distilled water and dried at 120 °C. The product was calcined at 600 °C for 4 hours to obtain H-SAPO-34.

Characterization

The powder XRD pattern was conducted on a PANalytical X'Pert PRO X-ray diffractometer with Cu K α radiation ($\lambda = 1.54059 \text{ \AA}$, 40 kV, 40mA). The crystal morphology was obtained using field emission scanning electron microscopy (Hitachi SU8020). The chemical compositions of samples were determined by X-ray fluorescence (XRF) spectrometer (Philips Magix-601). Nitrogen adsorption-desorption experiments were measured at 77 K on Micromeritics ASAP 2020.

¹²⁹Xe NMR, ¹²⁹Xe MAS NMR and 2D EXSY NMR

Before NMR experiment, a known amount of calcined SAPO-34 molecular sieve was dehydrated on a vacuum line at 673 K for 12 h and subsequently was transferred into the bottom of 5 mm outer diameter NMR tube (ID: 3.5 mm; Wilmad-LabGlass) with pressure valve in glove box. Subsequently, a sealed quartz tube (outer diameter of ca. 3 mm) was placed in the top of sample in order to reduce dead volume as much as possible (see Scheme S1). After degassing overnight at 393 K, a known amount of xenon was condensed quantitatively into NMR tube under liquid nitrogen on a homemade uptake apparatus. And the tubes were sealed off under equilibrium condition. After xenon adsorption, the tube was

sealed and equilibrated at room temperature. All data were acquired at equilibrium condition. The change of pressure sensor represents the amount of adsorbate in the samples. The loading of adsorbed xenon at low pressure was calculated by the ideal gas equation. The loading of adsorbed xenon at high pressure was calculated by using adsorbed xenon at very low pressure as an external standard. The sample used for ^{129}Xe MAS NMR was prepared by transferring sample in 5 mm NMR tube with xenon loadings of 3.6 per cage (which has equilibrated to 3 months) into 4 mm rotor in glove box. The loading of xenon in 4 mm rotor refers to the adsorbed xenon in 5 mm NMR tube with xenon loadings of 0.9 per cage.

^{129}Xe NMR measurements were run on a Bruker Avance III 600 MHz spectrometer operating at a frequency of 163 MHz for ^{129}Xe . One pulse sequence with 10 s recycle delay and 120 scans was used for ^{129}Xe NMR. ^{129}Xe MAS NMR experiments were performed on a Bruker Avance III 600 MHz spectrometer equipped with a 4 mm double resonance probe with spinning rate of 4 kHz and 8 kHz. Typically, ^{129}Xe MAS NMR spectra were acquired using single pulse sequence with 10 s recycle delay and 80 scans. 2D EXSY NMR spectra were acquired with $\pi/2-t_1-\pi/2-t_{\text{mix}}-\pi/2-t_2$ pulse sequence in the mixing time range of 0.2 to 100 ms. 32 and 256 point were used for the t_1 and t_2 dimension, respectively. Diluted xenon gas was used as the chemical shift reference at 0 ppm.

Pulsed field gradient (PFG) NMR

^{129}Xe PFG NMR experiments were performed on a Bruker Avance III 600 MHz spectrometer equipped with a 5 mm diff50 diffusion probe with the maximum gradient amplitude of 1800 G/cm in the z-direction. A bipolar-gradient stimulated echo sequence (13-interval sequence)³ was adopted in diffusion measurements to eliminate the effect of magnetic susceptibility in the beds of porous materials. Typically, the spin-echo attenuation $I(g)/I(0)$ could be obtained by linearly increasing gradient strength g in 16 steps, while gradient duration δ and diffusion time Δ keep constant in PFG NMR experiment. Optimal parameters (δ , Δ and g) were set for each sample in the PFG NMR measurements, respectively. The intracrystalline self-diffusion coefficient D can be obtained by the Eq. (1)^{4,5}

$$I = I_0 \exp \left[-(\gamma \delta g)^2 D \left(\Delta - \frac{\delta}{3} \right) \right] \quad (1)$$

where I and I_0 is the signal amplitudes with and without g , respectively. γ is the gyromagnetic ratio of the nucleus, δ is the effective gradient pulse duration, g is gradient strength, Δ is the diffusion time.

Monte Carlo simulation

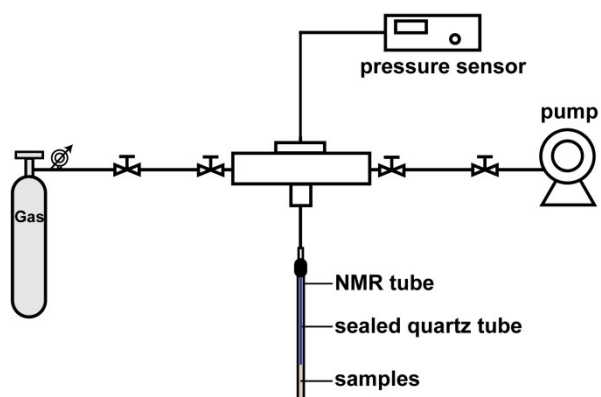
The grand canonical Monte Carlo (GCMC) simulation was performed in the canonical ensemble (NVT). The initial framework structures of pure silicon molecule sieve were taken from the International Zeolite Associations (IZA) database,⁶ then subsequently were substituted by Al and P atoms and optimized by GULP⁷ with SLC core-shell force field.⁸ The selected super cell was $2 \times 2 \times 2$. All interactions for xenon-xenon and xenon-framework were modeled using universal force field,⁹ which have been widely applied in zeolites system.^{10,11} A cutoff radius was set to 12.8 Å for the Lennard-Jones (LJ) interactions. During Monte Carlo

simulations, move types of exchange, conformer, rotation, translation and regrowth with probabilities of 39.2%, 19.6%, 19.6%, 19.6% and 2.0% were used, respectively. For each stat point, GCMC simulation consists of 1.0×10^7 steps to guarantee the equilibration, followed by 1.0×10^7 steps to sample the desired thermodynamics properties. The simulations were performed with Sorption module in the Material Studio software 7.0 and completed in SINOPEC Shanghai Research Institute of Petrochemical Technology.

References

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Results



Scheme S1 A schematic diagram of the uptake apparatus. An amount of SAPO-34 molecular sieve was loaded in the bottom of NMR tube and a sealed quartz tube was placed on the top of sample.

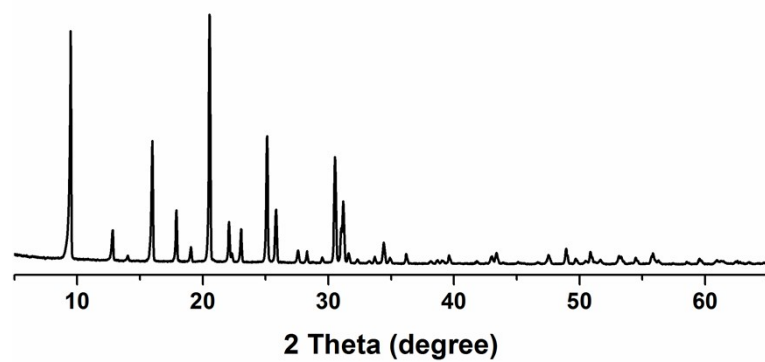


Fig. S1 XRD pattern of large crystal SAPO-34 molecular sieve.

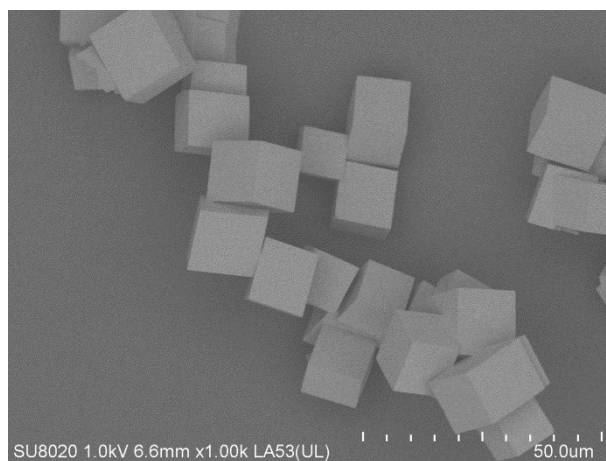


Fig.S2 SEM image of large crystal SAPO-34 molecular sieve.

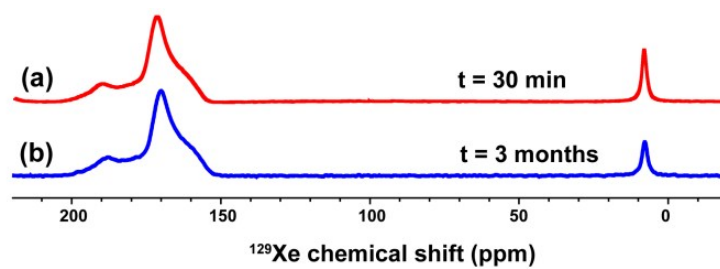


Fig. S3 ^{129}Xe NMR spectra of SAPO-34 with the loading of 3.6 xenon atoms per cage at different equilibration times (a) 30 min (b) 3 months at 298 K, respectively.

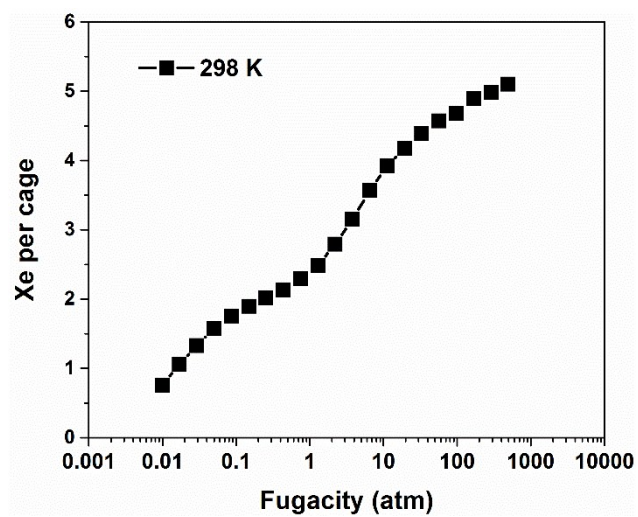


Fig. S4 GCMC stimulated adsorption isotherm of xenon atoms in CHA at 298 K.

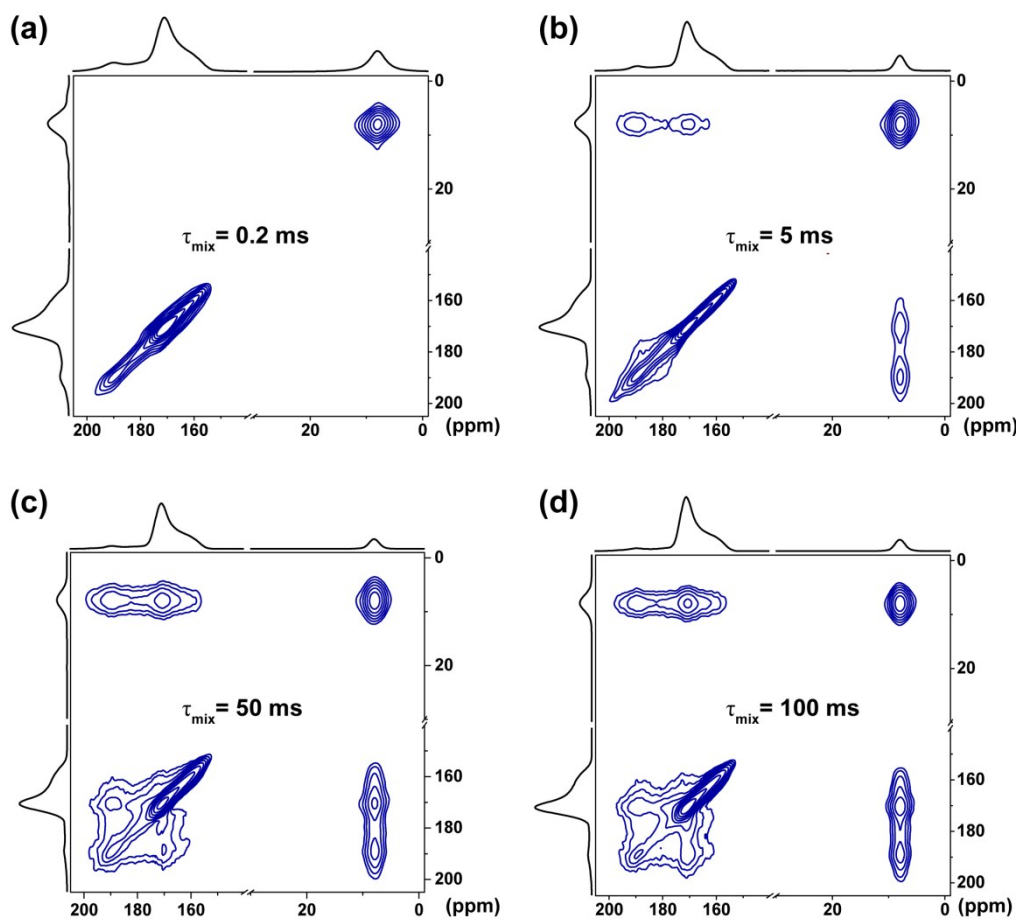


Fig. S5 2D EXSY NMR spectra of xenon adsorbed within SAPO-34 loaded with average loading of 3.6 xenon atoms per cage at 298 K with various mixing times of 0.2 ms (a), 5 ms (b), 50 ms (c), 100 ms (d).

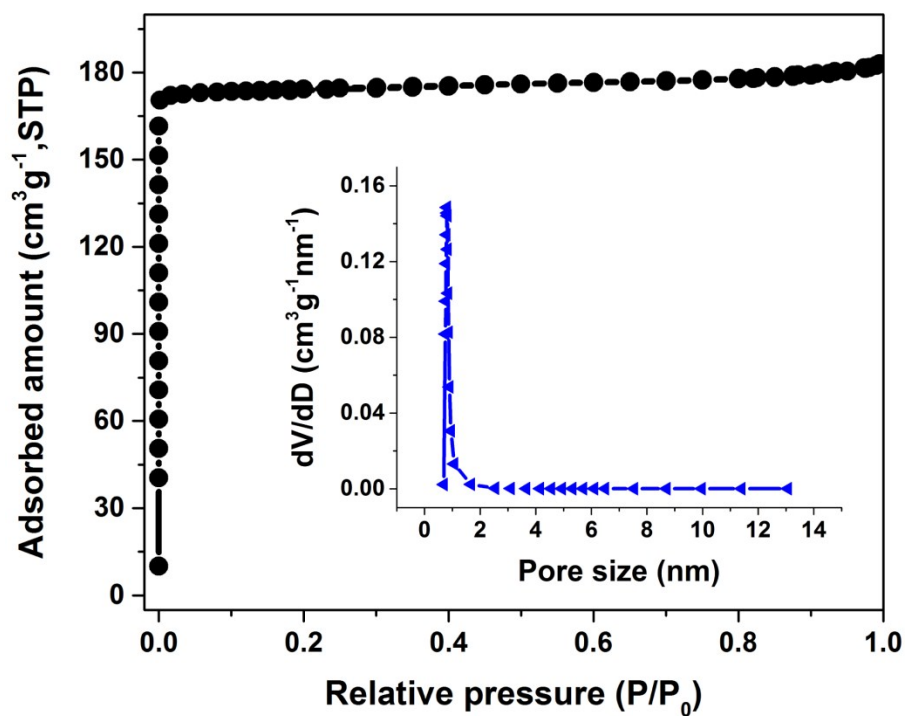


Fig. S6 N₂ adsorption-desorption isotherms of SAPO-34 with crystal size of 15 μm. The inset is the pore size distribution calculated from the adsorption branch.

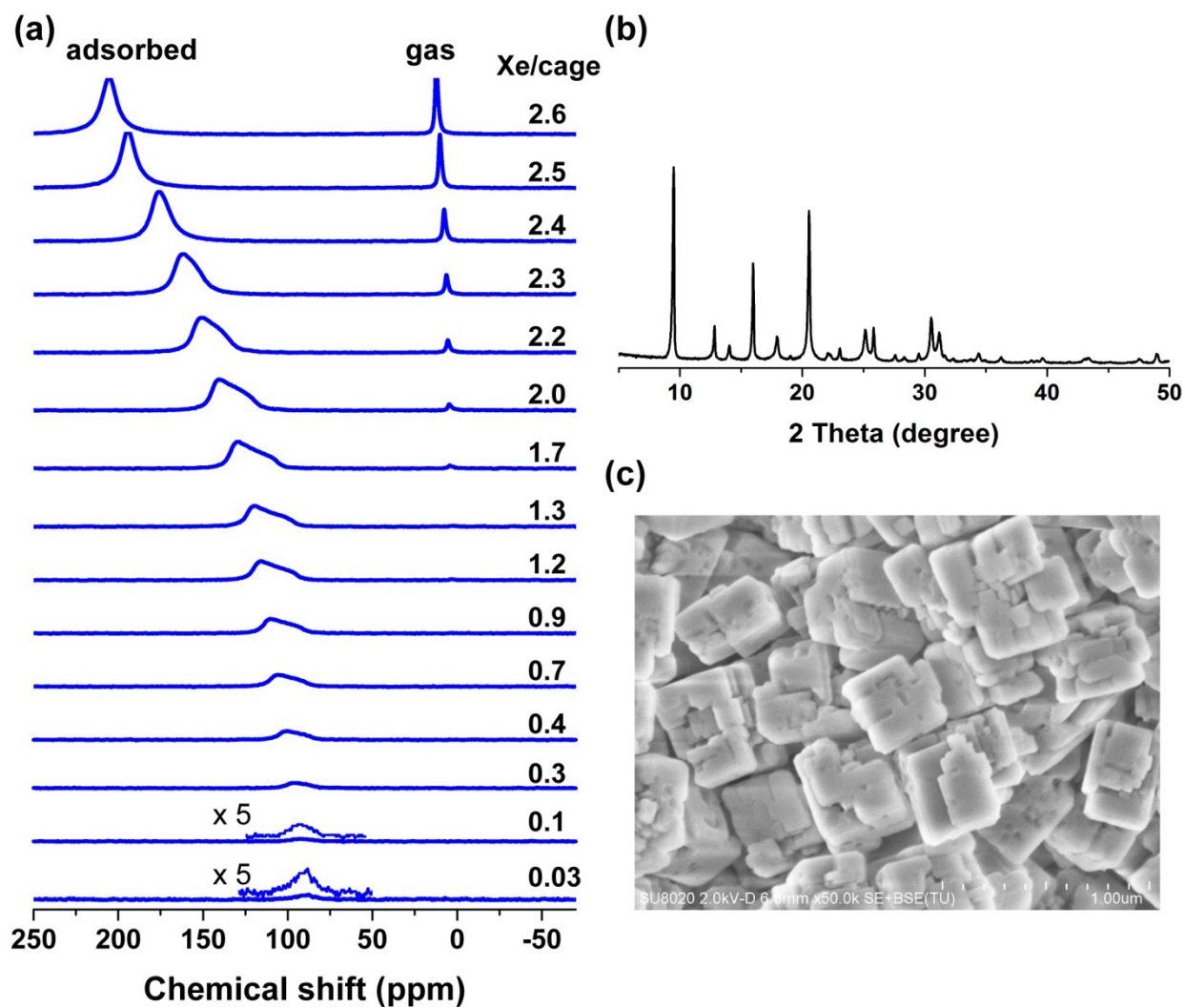


Fig. S7 (a) Loading-dependent ^{129}Xe NMR spectra of SAPO-34 with crystallite size of 400 nm at 298 K. (b) XRD pattern and (c) SEM image of the nanosized SAPO-34 molecular sieve.

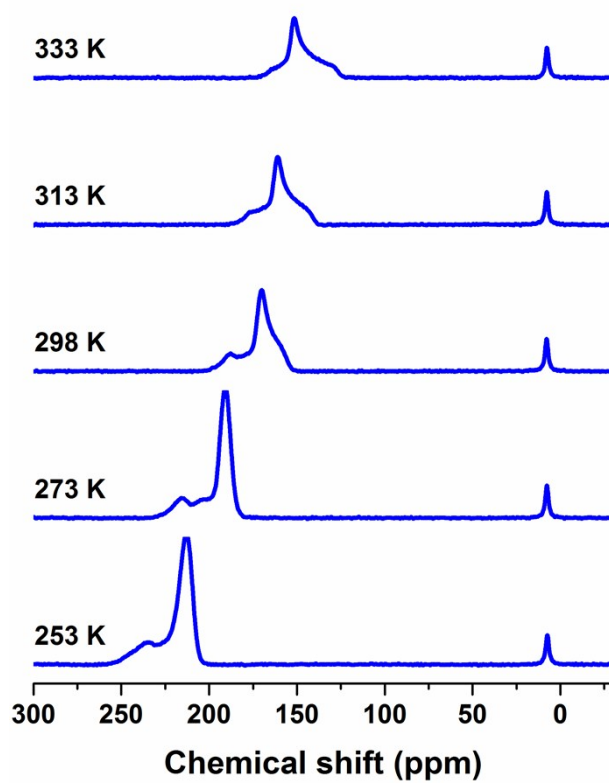


Fig. S8 Temperature-dependent ^{129}Xe NMR spectra of large crystal SAPO-34 with average loading of 3.6 xenon atoms per cage recorded at the temperature range of 253-333 K.

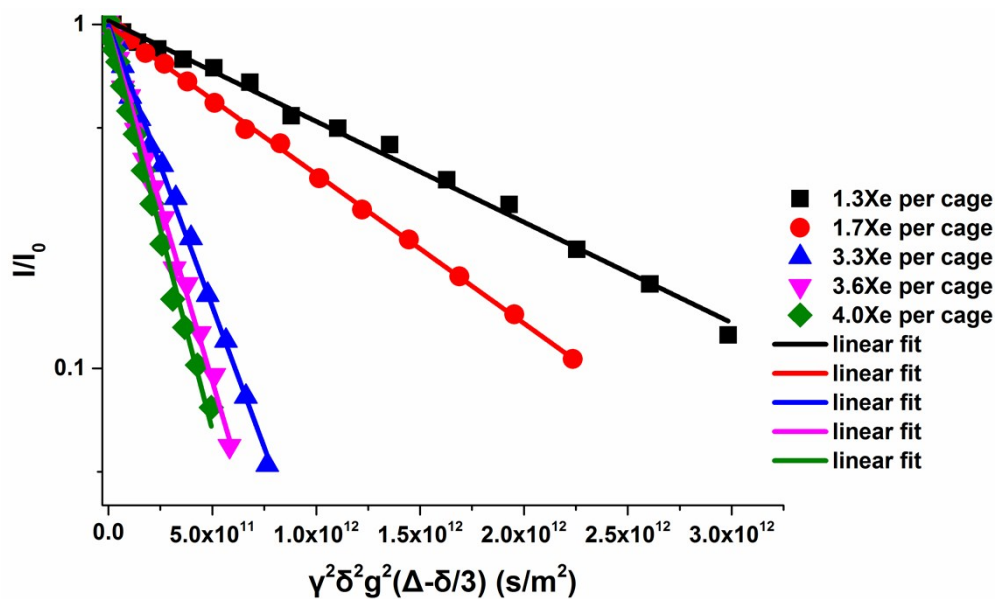


Fig. S9 Semi-logarithmic plots of ^{129}Xe PFG NMR spin-echo attenuation $I(g)/I(0)$ of xenon inside SAPO-34 molecular sieve loaded with average 1.3, 1.7, 3.3, 3.6 and 4.0 atoms per cage as a function of $\gamma^2 \delta^2 g^2 (\Delta - \delta/3)$ recorded at 298 K, respectively. Test conditions: gradient pulse duration of $\delta = 1.2$ -1.8 ms, diffusion time of $\Delta = 110$ -550 ms, gradient strength of $g = 36$ -1700 G/cm. The shown solid lines are the fitting curves with Eq. S1.

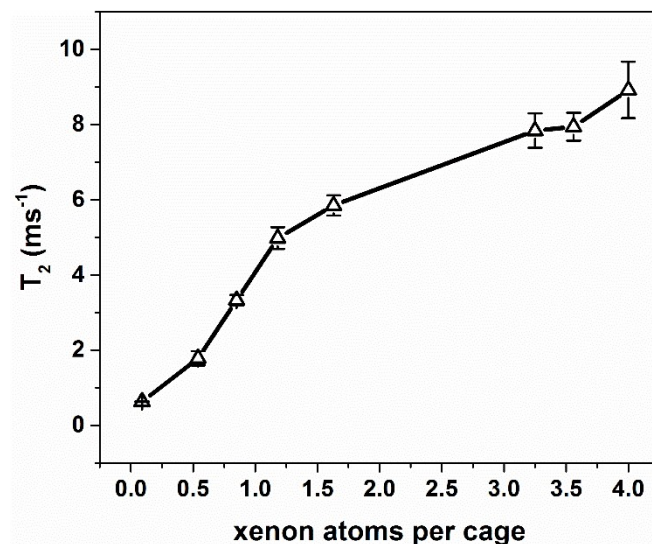


Fig. S10 Loading-dependent transverse relaxation time (T_2) of xenon in SAPO-34 molecular sieves at 298 K. The error bars are based on the standard errors and marked on all the symbol.

Table S1. Physicochemical properties of SAPO-34 molecular sieves.

Sample	Molar composition ^a	Surface area (m ² /g)		Pore volume (cm ³ /g)		Crystallite Size
		S _{BET} ^b	S _{micro} ^c	V _{total} ^d	V _{micro} ^e	
SAPO-34	Al _{0.468} P _{0.389} Si _{0.144}	604	599	0.30	0.29	15 μm
	Al _{0.520} P _{0.394} Si _{0.086}	575	542	0.36	0.27	400 nm

^a determined by X-ray fluorescence (XRF). ^b BET surface area. ^c Micropore area and ^e micropore volume determined from the t-plot method. ^d V_{total} is determined from the adsorbed volume at P/P₀ = 0.98.

Table S2. The proportion of occupied cages in different region and corresponding thickness of each region in a single crystal.

peaks	1	2	3	4
Chemical shift (ppm)	102	104	108	113
Xe _n clusters	Xe ₂	Xe ₃	Xe ₄	Xe ₅
Area proportion (%)	45.6	36.9	14.1	3.4
Number of occupied cages in a single crystal	0.456*m /2	0.369*m /3	0.141*m /4	0.034*m /5
Utilization ratio ^a	$n/N= m*(0.456/2+0.369/3+0.141/4+0.034/5)/(m/1) = 0.39$			
Total volume of occupied cages in a single crystal (um ³) ^b	15*15*15*0.39=1316			
Total volume of unoccupied cages in single crystal (um ³)	2059			
Total number of occupied cages in a single crystal	0.39*N			
Proportion of occupied cages in total occupied cages (%)	0.456/2/0.39 =58.0	0.369/3/0.39 =31.3	0.141/4/0.39 =9.0	0.034/5/0.39 =1.7
Volume of occupied cages in a single crystal (um ³)	1316*0.58 =763	1316*0.313 =412	1316*0.09 =118	1316*0.017 =22
Length of unoccupied cage region in a single crystal (um)	$2059^{-3}=12.72$			
Length of each occupied region in a single crystal (um) ^c	14.13	14.79	14.97	15
Thickness each occupied region in a single crystal (um)	0.71	0.33	0.09	0.02

^a The average number of xenon is about one per cage. The number of occupied cage in single crystal is defined as n. The total number of cage in single crystal is defined as N. The total number of xenon in single crystal is m.

^b SAPO-34 crystal is defined as cubic with a side length of 15um; Total volume of a single crystal of 15*15*15

^c An essential assumption of this quantification is that each region has same Xe_n clusters and all cages are occupied in this region.

