Article

A High-pressure NMR Tube for PFG Diffusion Studies: Revealing the Specific Confinement in RHO Zeolite

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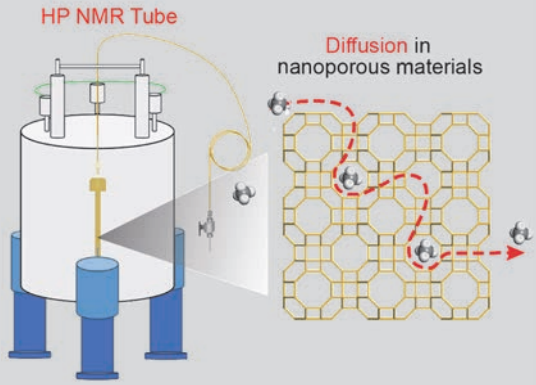
Diffusion is ubiquitous in nature and many technological processes, particularly in catalysis and gas separations using nanoporous materials. Interpreting the loading dependence of the self-diffusion coefficient (D_{self}) of guest molecules in nanopores is imperative to understanding diffusion mechanisms. Pulse gradient field (PFG) NMR is a powerful technique for measuring the D_{self} of target molecules under various pressures. However, the maximum pressures of commercial NMR tubes (usually<14.0 bar, 1 bar= 101325 Pa) are not high enough to investigate in realistic conditions or a wider pressure range. Herein, we developed a high-pressure tube (HP tube, up to 120 bar) for accurate D_{self} measurements, particularly in nanoporous material systems, featuring rapid sample loading and recovery. This HP tube bypasses the pressure-resistant design of diameter reduction and is equipped with a suite of sample fill tools, facilitating quick solids loading and non-destructive recovery. Its application to methane diffusion in DNL-6 (RHO) molecular sieve reveals the specifically confined diffusion, highlighting the confinement effect of the d8r structure. The HP NMR tube was confirmed to be a safe and reliable solution for high-pressure diffusion investigation *via* PFG NMR. This contribution advances molecular transport understanding and enables researchers to optimize materials for energy and catalysis technologies.



Keywords Diffusion; Porous material; Pulse gradient field (PFG) NMR; High-pressure NMR tube; Confinement effect

1 Introduction

The study of diffusion behavior in nanoporous materials has gained significant attention due to its relevance in catalysis, gas storage and separation, and electronic chemistry.[1−8] A better understanding of this phenomenon will aid in optimizing and developing industrial applications of these materials. For this purpose, a number of different experimental techniques are nowadays available for determining the transport diffusivities. Pulsed field gradient (PFG) NMR is a widely utilized technique for determining the self-diffusion coefficient (D_{self}) of guest molecules in nanoporous materials, such as metal-organic frameworks (MOFs) and molecular sieves.[9,10]

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Since diffusion behavior is highly correlated with guest molecule concentration in confined spaces, investigating the loading dependence of the D_{self} value is a crucial way to provide deeper insights into the fundamental mechanisms of molecular diffusion in nanoporous materials.[11−14] Hence, there is growing interest in extending studies to higher pressures *via* developing safe, reliable, and user-friendly high-pressure NMR tubes. Even though some commercial manufacturers offer borosilicate glass tubes, which can support moderate pressure up to 14 bar (Norell™). These tubes, specifically used for high-resolution liquid-state NMR, do not match the "pressure-resistant" criterion. Moreover, the pressure-resistant design of these commercially available NMR tubes with reduced inner diameters complicates both the solid-sample loading and cleaning. In 1954, Benedek & Purcell[15,16] developed the first "autoclave" device adapted for high-pressure NMR spectroscopy, which reaches a very high pressure of 9—10 kbar. In this device, the sample and the radiofrequency coil are directly placed in a pressure-resistant non-magnetic vessel made of beryllium-copper alloy or a more resistant titanium alloy.[17−20] Nevertheless, this design is also unsuitable for solid samples, due to low

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sensitivity, device assembly complexity, and the inconvenience of sample loading.

This work develops a high-pressure NMR tube, named HP-PFG-N, specifically designed for PFG NMR measurements in nanoporous material systems. The improved design and complementary sample loading tool facilitate quick sample filling, reaching a maximum pressure tolerance of at least 120 bar. Additionally, this design achieves non-residue recovery of solid powders (no sample residue remains in the NMR tube), eliminating the necessity for cleaning procedures. Applying this tube to investigate methane diffusion behavior in the DNL-6 molecular sieve, we experimentally confirmed the specific confinement effect of the d8r structure, consistent with prior studies[21−23] and our previous computational predictions.[1] The HP-PFG-N NMR tube is thus validated as a safe and reliable solution for high-pressure diffusion studies *via* PFG NMR. Its application enables researchers to explore new diffusion behaviors, decipher mechanisms, and optimize materials for energy storage, environmental applications, and industrial catalysis.

2 Experimental

2.1 Materials and Characterization

The large-grained DNL-6 molecular sieve was synthesized using the traditional hydrothermal method from the initial gel ratios of 2.0DEA:1.0Al_2O_3:0.8P_2O_5:0.4SiO_2:0.11CTAB:100H_2O.[24,25] Typically, aluminum isopropoxide and deionized water were mixed in a glass beaker, and then orthophosphoric acid (85%, mass fraction) and tetraethyl orthosilicate (TEOS) were added. After stirring for 1 h, an aqueous solution of cetyltrimethylammonium bromide (CTAB) was added, with the final addition of diethylamine (DEA) template. Stirring was kept during all the above mixing procedures. After several hours of stirring, the final homogeneous mixtures were transported into Teflon-lined autoclaves and crystallized at 200 °C under rotation conditions for 24 h. After crystallization, the autoclaves were cooled down, and the solid product was recovered by centrifugation, washed with deionized water repeatedly, and dried at 110 °C overnight. To avoid the hydrolysis of H-formed samples in the ambient atmosphere, all samples were freshly calcined at 550 °C for 6 h to remove the organic template before measurements.

The powder XRD patterns were recorded for phase identification by using a PANalytical X'Pert PRO X-ray diffractometer with Cu $K\alpha$ radiation (λ=0.154059 nm) operating at 40 kV and 40 mA. The crystal morphology and particle size of the catalysts were measured by a field emission scanning electron microscope (TM3000).

2.2 Sample Preparation

2.2.1 Dehydration and Packing

Before diffusion tests, all freshly calcined samples were dehydrated on a vacuum line (<10^{-3} Pa) *via* a stepwise procedure to a final temperature of 693 K for 12 h. After activation, known amounts of materials were transferred into the inner capillary tube *via* a home-made plastic funnel with a densification tool and placed at the bottom of the HP-PFG-N NMR tube with a sealed quartz tube (outer diameter of *ca*. 2.7 mm) under an Ar atmosphere in a glove box. Then, the NMR tube cap was tightened with the stainless steel ball valve closed to isolate the sample from the ambient air. Finally, the HP NMR tube was taken out of the glove box and prepared for gas loading.

2.2.2 Gas Filling and Sample Recovery

The methane-loaded samples used for PFG NMR were prepared by controlling the adsorption pressures of methane in the HP-PFG-N NMR tubes on the vacuum line. Detailed procedures are introduced as follows.

(1) Ar gas replacement. The sample-loaded HP-PFG-N NMR tube was connected to the vacuum line by connecting the stainless-steel ball valve on the tube to the stainless-steel tubing in the vacuum line. Then, the inert gas was pumped out using the transition chamber by performing multiple evacuations, thereby avoiding sample displacement during the process. *In-situ* heating of the HP-PFG-N NMR tube up to 120 °C was performed and kept for more than 2 h to desorb any residual gases, ensuring a clean internal environment.

(2) Target gas filling. Firstly, the stainless-steel ball valve of the HP-PFG-N NMR tube was closed, and a certain amount of the target gas was filled into the pressurization transition line up to a relatively low pressure. Secondly, the gas cylinder output valve was closed to stabilize the line pressure, and the ball valve of the HP-PFG-N NMR tube was turned on to allow gas to enter. Repeat this step several times, gradually increasing the pressure inside the NMR tube until the desired target pressure is reached.

(3) Adsorption equilibrium. The methane-loaded samples in NMR tubes are sealed off and equilibrated at room temperature for at least 1 h. Record the pressure gauge reading after equilibrium.

(4) Disconnect the HP-PFG-N NMR tube. Close the ball valve of the NMR tube and slowly release the residual pressure in the transition line to avoid sudden decompression. Disconnect the NMR tube assembly from the sealing valve.

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(5) Recovery. After testing, reconnect the NMR tube assembly to the vacuum line. Use the pressurization transition section to perform multiple slow depressurization steps, ensuring the pressure differential is minimized to avoid the impacts of gas flow to the connectors, tube, and sample. Once depressurization was complete, unscrew the NMR tube cap to pour out the sample, enabling non-destructive recovery.

2.3 NMR Experiments

NMR measurements were conducted on a Bruker AVANCE III 600 spectrometer, equipped with a 14.1 T wide-bore magnet. A 5 mm diff50 probe was used, providing the maximum gradient strength of 1800 G/cm in the *z*-direction. The coiled 1/16'' PEEK extension tubing of the HP-PFG-N NMR tube was unwound before inserting the NMR tube. Lifting gas was not used in placing and lifting the HP NMR tube, and the NMR tube body was suspended by the 1/16'' PEEK extension tubing and gradually lowered into the right position of the magnet with the stainless steel ball valve placed in the safety zone far away from the magnet. ^{1}H chemical shift was referenced to the prepared H_2O (1% H_2O in D_2O, plus 0.1% $CuSO_4$) at δ 4.8.

2.3.1 1D ^{1}H NMR

A single pulse sequence with a ^{1}H radio frequency (RF) field strength of 19 kHz was applied, and the number of scans and recycle delay were 16 and 10 s, respectively. A spin echo sequence was also used to eliminate the background signals from the probe and PEEK materials for comparison, with a ^{1}H RF of 21 kHz, a refocused time of 1 ms, 16 scans, and a recycle delay of 10 s.

2.3.2 ^{1}H PFG NMR Measurement

A bipolar-gradient stimulated echo sequence (STEBP)[26] was applied in ^{1}H PFG NMR diffusion measurements to eliminate the effect of magnetic susceptibility in the bed of material. Optimal parameters (δ, g, and Δ) were set for each PFG NMR test. The intracrystalline self-diffusion coefficient, D, is determined using Eq. 1

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

where I and I_0 are the signal amplitudes with and without gradient field strength, respectively. The echo signals decayed exponentially as the gradient strength (g) increased linearly, while the diffusion time (Δ) and effective gradient pulse duration (δ) remained constant. γ is the gyromagnetic ratio of the ^{1}H nucleus. For the measurement under a pressure of 6.4 bar, the g was from 100.1 G/cm to 800.7 G/cm, δ was 0.630 ms, and Δ was 5.00 ms. For the measurement under a pressure of 103.5 bar, the g was from 100.1 G/cm to 1000.0 G/cm, δ was 0.690 ms, and Δ was 5.00 ms.

3 Results and Discussion

3.1 NMR Tubes for Pressure Systems

3.1.1 Commercial Pressure Valved NMR Tubes

Present commercially available pressure-resistant NMR tubes are not specifically designed for PFG NMR measurements, but are primarily applied in gas or gas-liquid mixed systems. Such NMR tubes need to ensure not only excellent airtightness but also meet stringent requirements for material purity, including minimal ^{1}H nuclear background signals, as well as exhibit outstanding chemical inertness and resistance to chemical corrosion. In typical designs shown in Fig. 1, the sealing valve is placed at the top of the NMR tube, which is generally fabricated using polytetrafluoroethylene (PTFE) fluoropolymer, an inert material that resists virtually all solvents, reactive chemicals, and deterioration induced by corrosive conditions. The body of the NMR tube (tube wall) adopts a low-expansion borosilicate glass, which matches the tube's expansion coefficient, minimizing the risk of joint failure caused by internal strain or thermal shock. Moreover, Borosilicate glass can tolerate a maximum temperature of about 230 °C, resists sudden temperature changes or thermal shock, and possesses minimal background signals as negligible NMR signals from nuclei, such as ^{1}H and ^{13}C.

Fig. 1 displays valved NMR sample tubes designed for intermediate pressure (Fig. 1, A and C, numbered CT1) and high pressure (Fig. 1, B and D, numbered CT2), respectively, presented by the **NORELL** Inc. For the CT1, the ferrule or sealing nut (included with the valve), used to seal the pressure supply tubing to the valve, is constructed from ethylene-tetrafluoroethylene (ETFE) fluoropolymer, which also displays outstanding corrosion, chemical resistance, and mechanical properties such as toughness, high impact strength, and long flex life. The compression nut (also included with the valve) is machined from polyether ether ketone (PEEK), a high-performance polymer known for its exceptional tensile strength, stiffness, dimensional stability, and chemical resistance. This durable material ensures reliable performance and longevity across repeated connection and disconnection cycles. The CT2 tube achieves higher pressure resistance through improved designs, including the adoption of a thicker glass wall, a narrowed tube inner diameter (I.D.) at the sealing port (flow passage), multi-layer perfluoroelastomer O-rings, and a tightly matched thread between the PTFE valve plug and the glass valve shell. The tightly matched thread increases the

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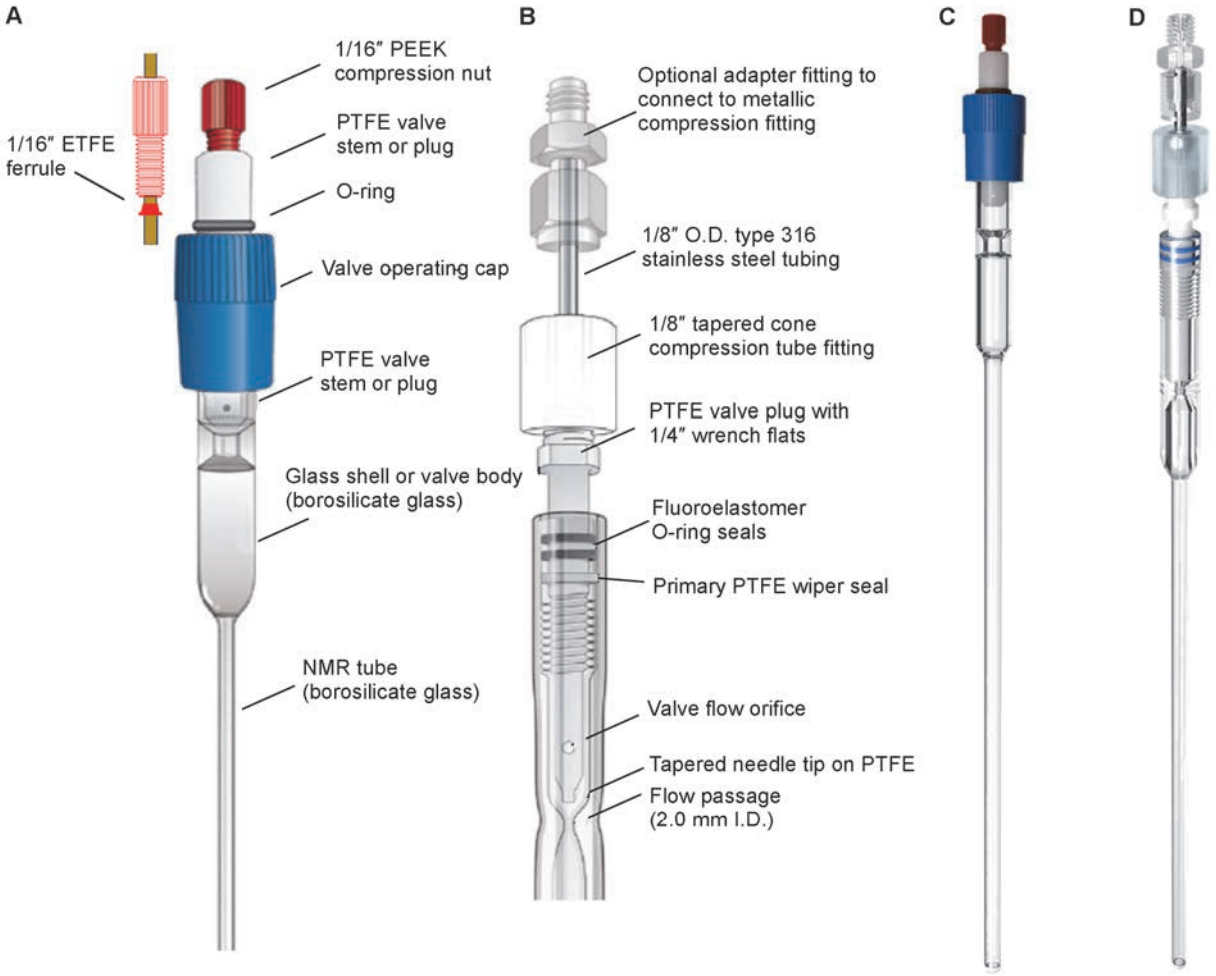

Fig. 1 Schematic (A, B) and experimental (C, D) views of the high-pressure valved NMR sample tube designed by NORELL, Inc.

(A, C) Valved NMR sample tube for intermediate pressure; (B, D) high-pressure valved NMR sample tube for high pressure. O.D. represents outer diameter, and I.D. represents inner diameter.

maximum force of the valve, and the reduced flow passage decreases the force-bearing area. Hence, these improvements enhance the maximum pressure of the NMR tube. However, the reduced flow passage significantly hinders the filling and recovery of solid powder samples, thereby limiting its application in PFG NMR testing, although this design imposes no limitation on the flow of gases and liquids. Furthermore, the maximum pressure tolerance of commercially available high-pressure NMR tubes is generally below 14 bar, which is insufficient for diffusion coefficient measurements under broader pressure ranges or conditions closer to real-world scenarios.

3.1.2 HP-PFG-N NMR Tube for PFG NMR Measurements

Considering the numerous limitations of commercial NMR tubes in diffusion research, the development of NMR tubes capable of supporting PFG NMR measurements under high-pressure conditions, particularly for solid porous material diffusion studies, has become imperative. Fig. 2 displays the HP-PFG-N NMR tube designed for PFG NMR measurement and the complementary sample loading tools. Table 1 briefly compares the current design with commercially available HP NMR tubes (CT1 & CT2 introduced above) on some key metrics. Compared to the commercially high-pressure valved NMR tube (Fig. 1), the HP-PFG-N NMR tube adopts a separate sealing strategy so that the core sealing valve can be extended to the exterior of the magnet. This strategy circumvents the conventional integration of the valve and NMR tube. Instead, the valve and NMR tube body are connected through a pressure-resistant PEEK tubing material, permitting the use of commercial valves, such as stainless-steel ball valves, resulting in safer and more straightforward sample preparation operations. Excluding the commercial valve and connectors, extension tubing and tube body also apply the PEEK material to achieve high-pressure resistance. As a semicrystalline thermoplastic with

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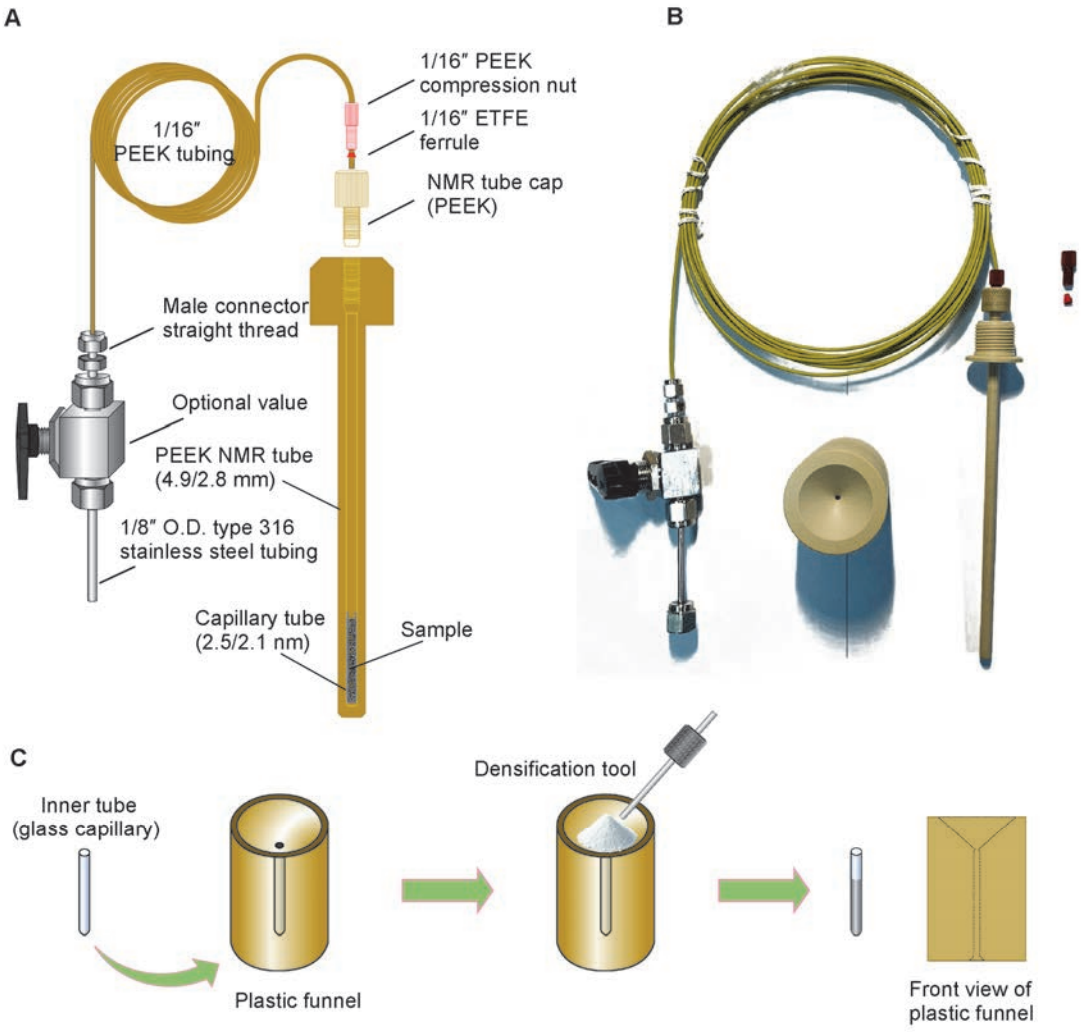

Fig. 2 HP-PFG-N NMR tube for diffusion study and complementary sample loading tools

Table 1 Comparative table: commercially available HP NMR tubes *vs*. HP tube (HP-PFG-N) in this work

NMR Tube	CT1 (MW-IPV)	CT2 (EX1-HPV)	HP-PFG-N
Use cases	Liquid or powdered sample	Liquid/restricted use for powdered samples	Powdered or liquid sample
Body material	Borosilicate glass	Borosilicate glass	PEEK
Pressure/bar	<9	<14	<120
Temperature/°C	<230	<260	<260
I.D./mm (O.D.≈4.9)	3.43	2.20/2.00	2.80
Comple-mentary tools	None	None	Sample loading tools
Sample loading/recovery	Simple/ Moderate	Arduous/ Arduous	Easy/easy
Tube clean	Moderate	Arduous	Contami-nation-free
Mechanical durability	Fragile	Fragile	Durable
Safty	Laceration hazard	Laceration hazard	Safe
Cost	*ca*. $ 285	*ca*. $ 490	*ca*. $ 260

excellent mechanical and chemical resistance properties, PEEK is retained to high pressure (tensile strength of 90 MPa to 100 MPa) and high temperatures (a glass transition temperature of around 143 °C). In contrast to well-applied glass, this material will not generate sharp fragments even in the event of accidental rupture, reducing the risk of serious injuries to operators. Due to the separated design with the stainless-steel ball valve and PEEK material, the maximum pressure tolerance of the HP tube is up to 120.0 bar, and its operating temperature reaches a range of –60—260 °C. Besides, the pressure-reducing tapered structure (*i.e.*, tapered needle tip on PTFE and the reduced flow passage of 2.0 mm I.D.) in the commercial NMR tube shown in Fig. 1, designed for mitigating stress on connecting

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components, is eliminated. Instead, a uniform inner diameter flow passage is adopted to streamline sample filling and recovery. Nevertheless, directly packing solid samples into the NMR tube is not recommended, as powdered specimens tend to adhere to the inner walls, making post-experiment cleaning particularly challenging for such a narrow and elongated container. As illustrated in Fig. 2C, the NMR tube is accompanied by a sample-loading accessory. The sample is transferred into a capillary tube using a funnel, ensuring tube-contact-free delivery and preventing surface adhesion of the tube wall. The capillary tube can be constructed from glass, plastic, or other materials without pressure resistance requirements. This design facilitates the sample-loading process, enables non-residue sample recovery, and eliminates the need for tube cleaning. During testing, the coiled tubing is unrolled to extend the stainless-steel valve into a safe area outside the magnetic field.

3.2 Diffusion Measurement on HP-PFG-N NMR Tube

Furthermore, the HP-PFG-N NMR tube was applied to investigating the diffusion behavior of methane in DNL-6 molecular sieve (RHO topology, shown in Fig. 3A). XRD pattern and SEM image indicated the good crystallinity of DNL-6 molecular sieves with a crystallite size of approximately 6 μm (Fig. 3, B and C). Detailed procedures for sample preparation and operating instructions are introduced in the experimental section.

3.2.1 Tube Background and Measured System

Prior to PFG NMR measurement, the interference of ^{1}H NMR background signals should first be evaluated, due to replacing the conventional well-applied glass body of the NMR tube with organic PEEK material (molecular formula shown in Fig. 3D). As the black line in Fig. 3E, an empty NMR tube exhibits a broad hydrogen background under a static measurement condition using a single-pulse sequence, due to strong ^{1}H-^{1}H homonuclear dipolar interaction, wherein the asterisk and hash are from the backgrounds of the probe and the HP NMR tube, respectively. In contrast, after loading the DNL-6 molecular sieve sample into the tube and charging with 6.4 bar methane gas (green line), the signals of gaseous (δ 2.6), intercrystalline-adsorbed (δ 3.0), and intracrystalline-adsorbed methane (δ 2.3) are significantly narrower than the PEEK background signal, indicating fast CH_4 molecule motion. As a result, the background signal is not prominent. Moreover, the broader background signals are suppressed significantly using a spin-echo sequence (orange line) due to its short transverse relaxation time (T_2) compared to methane signals, only leaving the sample-specific signals. A combination of spin echo and pulse gradient field under the diffusion coefficient measurement, both signals of broad signals and rapidly diffusing gaseous methane become negligible (red line), only showing the sole target intracrystalline-adsorbed methane signal.

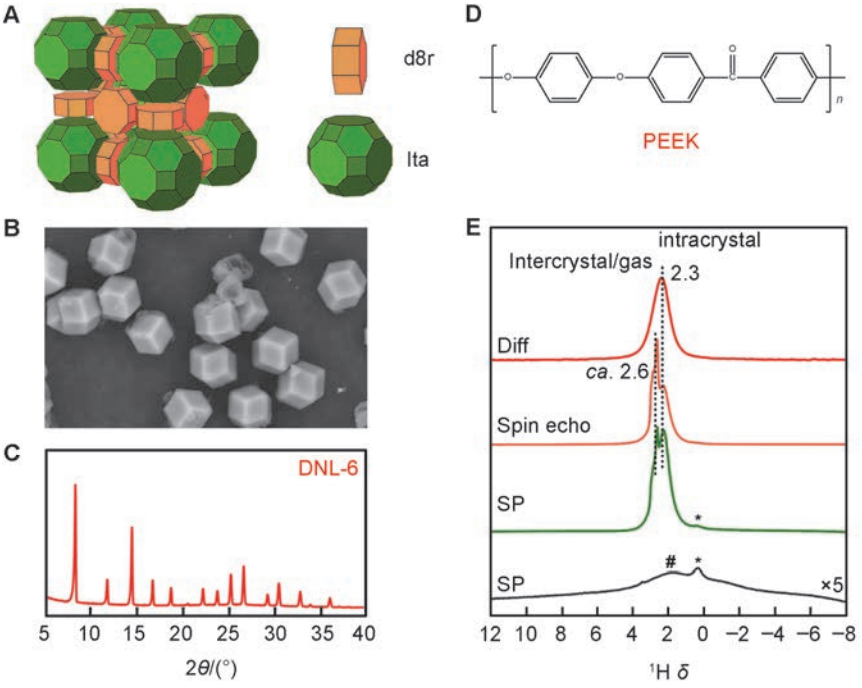

Fig. 3 3D models highlighted by dark green-filled lta cages and orange-filled d8r structures of RHO (A), SEM image (B), and XRD pattern of DNL-6 (C), molecular formula of PEEK material (D), and ^{1}H NMR spectra of empty HP-PFG-N tube (black line) and DNL-6 sample filled with methane gas in HP-PFG-N tube using different sequences (E)

3.2.2 Methane Diffusion in DNL-6 Molecular Sieves

To further validate the feasibility of applying the HP-PFG-N NMR tube in diffusion studies. It is used to investigate the diffusion behavior of methane in DNL-6 molecular sieve. Our previous works[21−23,27] have demonstrated that the d8r structure of RHO topology showed specific confinement effort for small guest molecules (such as Xenon and CH_3OH) adsorption and diffusion behaviors, as well as for coke growth. However, due to the smaller molecular size, the trend of methane diffusion rates with varying

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adsorption pressure is less pronounced within a limited pressure range. Thus, the utilization of the high-pressure NMR tube aims to reveal the definite tendency of CH_4 diffusion coefficients in DNL-6 molecular sieves as a function of pressure. As the 3D model displayed in Fig. 3A, DNL-6 is an RHO topology with a body-centered cubic symmetry structure, composed of large lta cages interconnected *via* short and narrow d8r channels. The bipolar-gradient stimulated echo sequence (STEBP) PFG NMR experiment used for the diffusion coefficient measurement is displayed in Fig. 4A, wherein parameters Δ, δ, g, and τ are diffusion time, gradient pulse width, gradient pulse amplitude, and inter-gradient delay, respectively. Even under high pressure of 103.5 bar, the HP-PFG-N NMR tube demonstrates excellent gas tightness, as the integral of the ^{1}H signals remains unchanged after more than 1 h of rest (not shown). The ^{1}H PFG NMR spectra of methane diffusing in DNL-6 molecular sieves measured at 6.4 and 103.5 bar at 298 K, as a function of linearly increasing gradient strength (g), are presented in Fig. 4, B and C, respectively. The conditions of 6.4 and 103.5 bar of methane are achieved using the HP-PFG-N NMR tube, whereas the 13.0 bar condition (almost the maximum operating pressure of present commercial NMR tubes) is conducted in a CT1. Due to the high gas filling pressure, all three tests manifest excellent signal-to-noise ratios (SNR) with shorter measurement time. The corresponding ^{1}H PFG NMR attenuations I/I_0 as a function of $\gamma^2\delta^2g^2(\Delta-\delta/3)$ are plotted in Fig. 4D on a log-linear scale. The data are well-fitted by Stejskal-Tanner (Eq. 1), confirming standard three-dimensional isotropic diffusion.[28] Fig. 4E displays the self-diffusion coefficients, D_{self}, of methane within DNL-6 molecular sieve that are 3.20×10^{-10}, 3.09×10^{-10}, and 1.83×10^{-10} m^2/s under 6.4, 13.0, and 103.5 bar, respectively, indicating a pronounced reduction in D_{self} with the methane loading increasing. Our previous work[23] has reported that Xe molecules are prone to adsorb in the more confined d8r space.

Likewise, d8r is also the favorable adsorption of methane in DNL-6 despite the smaller size of methane than Xe. As a result, more and more methane molecules prefer to occupy the d8r prisms, which serve as the mandatory pathway for guest molecules to diffuse between cages, impeding the intercavity motions inside the DNL-6 and decreasing the diffusivity with increasing the methane loading. Nonetheless, it is noticeable that the difference in D_{self} between 6.4 bar and 13 bar is minimal, though 13.0 bar is close to the maximum pressure resistance of commercially available NMR tubes and is double 6.4 bar. Measurements of methane diffusion with HP-PFG-N NMR under high-pressure conditions reveal a clear dependence of diffusion behavior on adsorption pressure.

Therefore, the HP-PFG-N NMR tube was confirmed to be a safe, accurate, and reliable solution for diffusion investigation in porous materials *via* PFG NMR, regardless of high or low pressure. This HP tube bypasses the pressure-resistant design of diameter reduction and is equipped with a suite of sample fill tools, facilitating quick solids loading

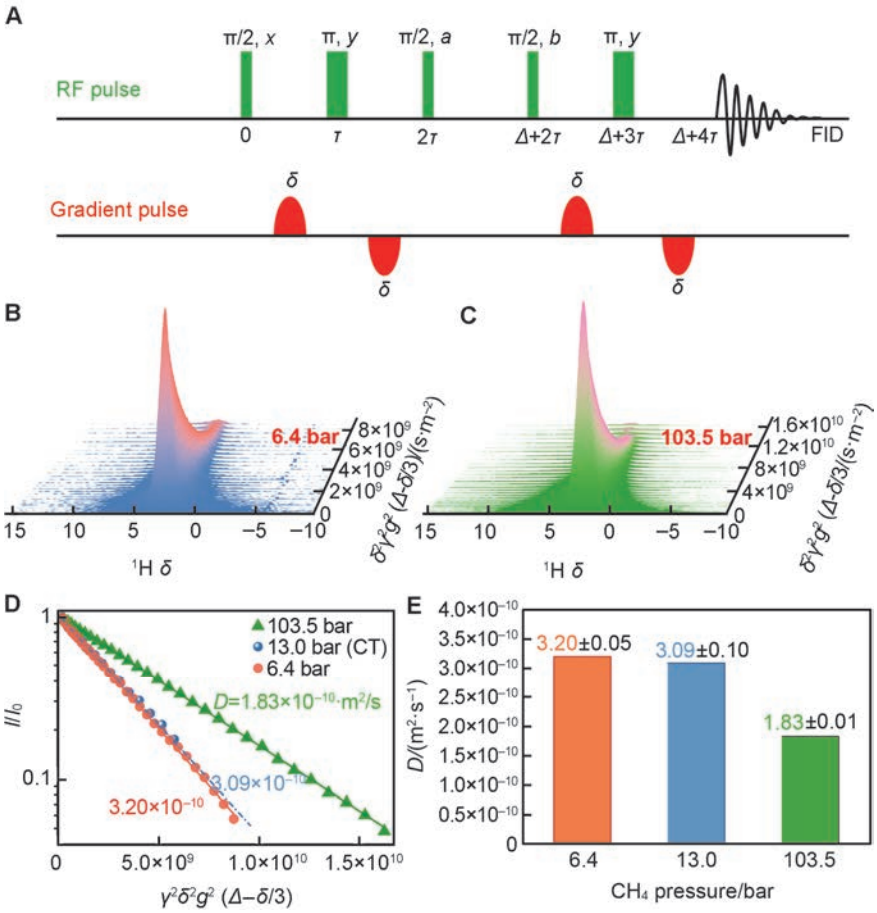

Fig. 4 Radio frequency and gradient pulse scheme of the bipolar-gradient stimulated echo sequence (STEBP) PFG NMR experiment (A), ^{1}H PFG NMR signals decay with linearly increasing gradient magnetic field strength for DNL-6 at 6.4 bar (B) and 103.5 bar (C) of methane, semilogarithmic plots of ^{1}H PFG NMR spin-echo attenuation I_g/I_0 of methane inside DNL-6 molecular sieves at 6.4, 13.0, 103.5 bar as a function of $\gamma^2\delta^2g^2(\Delta-\delta/3)$ recorded at 298 K, respectively (D), and loading dependence on the self-diffusion coefficient of methane adsorbed in DNL-6 at 298 K (E)

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and non-residue recovery. The D_{self} tendency of methane in the RHO topologic SAPO molecular sieve (DNL-6) was revealed, highlighting the confinement effect of the d8r structure. The application of the HP-PFG-N NMR tube, not only advances fundamental research on molecular transport, possible to enrich diffusion behaviors and decipher the diffusion mechanisms, but also supports the development of advanced materials for energy and catalysis technologies.

4 Conclusions

The HP-PFG-N tube bypasses the pressure-resistant design of diameter reduction and is equipped with a suite of sample fill tools, facilitating quick solids loading and non-residue recovery. Such an HP NMR tube typically operates within a temperature range of −60—260 °C. By incorporating commercially available valves and replacing fragile materials (glass or quartz) with robust PEEK material, it exhibits stable pressure resistance and enhanced mechanical durability. In addition, the D_{self} tendency of methane in DNL-6 molecular sieve was revealed by applying the HP-PFG-N NMR tube, highlighting the confinement effect of the d8r structure. As an example of methane diffusion in the DNL-6, the HP-PFG-N NMR tube was confirmed to be a safe and reliable solution for high-pressure diffusion investigation *via* PFG NMR. Its application not only advances fundamental research on molecular transport but also supports the development of advanced materials for energy and catalysis technologies.

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Conflicts of Interest

The authors declare no conflicts of interest.

References

[1] Liu Z. Q., Lou C. Y., Yuan J. M., Tang X. M., Fan Y. Z., Qi J., Zhang R., Peng P., Liu G. L., Xu S. T., Zheng A. M., *J. Am. Chem. Soc.*, **2025**, *147*, 6126.
[2] Brandani S., Hwang S., Kärger J., Mangano E., *Nat. Commun.*, **2024**, *15*, 5721.
[3] Zuo P. P., Ye C. C., Jiao Z. R., Luo J., Fang J. K., Schubert U. S., McKeown N. B., Liu T. L., Yang Z. J., Xu T. W., *Nature*, **2023**, *617*, 299.
[4] Yuan J. M., Gao M. B., Liu Z. Q., Tang X. M., Tian Y., Ma G., Ye M., Zheng A. M., *Nat. Commun.*, **2023**, *14*, 1735.
[5] Karger J., Freude D. Haase J., *Processes*, **2018**, *6*, 147.
[6] Karger J., Ruthven D. M., *New J. Chem.*, **2016**, *40*, 4027.
[7] Karger J., Valiullin R., *Chem. Soc. Rev.*, **2013**, *42*, 4172.
[8] Chmelik C., Kaerger J., *Chem. Soc. Rev.*, **2010**, *39*, 4864.
[9] Karger J., Pfeifer H., *Zeolites*, **1987**, *7*, 90.
[10] Cotts R. M., Hoch M. J. R., Sun T., Makert J. T., *J. Magn. Reson.*, **1989**, *83*, 252.
[11] Jakobtorweihen S., Verbeek M. G., Lowe C. P., Keil F. J., Smit B., *Phys. Rev. Lett.*, **2005**, *95*, 044501.
[12] Beerdsen E., Dubbeldam D., Smit B., *Phys. Rev. Lett.*, **2006**, *96*, 044501.
[13] Beerdsen E., Smit B., Dubbeldam D., *Phys. Rev. Lett.*, **2004**, *93*, 248301.
[14] Dubbeldam D., Beerdsen E., Vlugt T. J. H., Smit B., *J. Chem. Phys.*, **2005**, *122*, 224712.
[15] Benedek G. B., Purcell E. M., *J. Chem. Phys.* **1954**, *22*, 2003.
[16] Horvath I. T., Millar J. M., *Chem. Rev.*, **1991**, *91*, 1339.
[17] Ballard L., Reiner C., Jonas J., *J. Magn. Res.*, **1996**, *123*, 81.
[18] Ballard L., Yu A., Reiner C., Jonas J., *J. Magn. Res.*, **1998**, *133*, 190.
[19] Jonas J., *Biochem. Biophys. Acta,* **2002**, *1595*, 145.
[20] Jiri J., *High-Pressure Studies Using NMR Spectroscopy,* Academic Press (Elsevier Ltd.), Cambridge, MA, USA, **2010**.
[21] Lou C. Y., Zhang W. N., Ma C., Fan B. H., Xu S. T., Gao S. S., Guo P., Wie Y. X., Liu Z. M., *ChemCatChem*, **2021**, *13*, 1299.
[22] Gao S. S., Yuan J. M., Liu Z. Q., Lou C. Y., Yu Z. X., Xu S. T., Zheng A. M., Wu P. F., Wei Y. X., Liu Z. M., *J. Phys. Chem. C*, **2021**, *125,* 6832.
[23] Gao S. S., Liu Z. Q., Xu S. T., Zheng A. M., Wu P. F., Li B., Yuan X. S., Wei Y. X., Liu Z. M., *J. Catal.*, **2019**, *377*, 51.
[24] Su X., Tian P., Li J., Zhang, Y., Meng S., He Y., Fan D., Liu Z., *Micropor. Mesop. Mater.*, **2011**, *144*, 113.
[25] Yan N., Wang L., Liu X., Wu P. F., Sun T. T., Xu S. T., Han J. F., Guo P., Tian P., Liu Z. M., *Mater. Chem. A*, **2018**, *6*, 24186
[26] Karger J., *Chemphyschem*, **2015**, *16*, 24.
[27] Wang N., Zhi Y. C., Wei Y. X., Zhang W. N., Liu Z. Q., Huang J. D., Sun T. T., Xu S. T., Lin S. F., He Y. L., Zheng A. M., Liu Z. M., *Nat. Commun.*, **2020**, *11*, 1079.
[28] Karger J., *Chemphyschem*, **2015**, *16*, 24.