Development of *In Situ* MAS NMR and Its Applications in Material Synthesis and Heterogeneous Catalysis

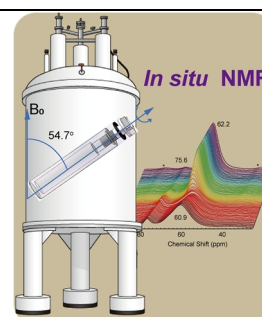Xinlong Yao[1,2], Zhenchao Zhao[3]* and Guangjin Hou[1]*

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ABSTRACT High-resolution magic angle spinning (MAS) NMR can afford both qualitative and quantitative information of the solid, liquid and gas phase at atomic level, and such information obtained at *in situ*/operando conditions is of vital importance for understanding the crystallization process of material as well as the reaction mechanism of catalysis. To meet the requirement of experimental conditions for material synthesis and catalytic reactions, *in situ* MAS NMR techniques have been continuously developed for using at higher temperatures and pressures with high sensitivity. Herein, we will briefly outline the development of this technology and discuss its detailed applications in understanding material synthesis and heterogeneous catalysis.

Keywords: *in situ* NMR, high-temperature high-pressure, material synthesis, heterogeneous catalysis, molecular sieves

n INTRODUCTION

The atomic-level understanding of the crystallization process of functional materials and molecular transformation process in catalysis is highly desirable for materials and catalysis science, which can facilitate the rational design and optimization of related processes. Whereas, the material synthesis or chemical reactions always proceed under certain pressure and temperature, and therefore, a variety of advanced *in situ* characterization techniques such as Raman, IR spectroscopy, X-ray diffraction, X-ray absorption spectroscopy, X-ray photon spectroscopy, solid-state NMR spectroscopy, scanning electron microscopy and transmission electron microscopy have been developed.[1-8] Solid-state MAS NMR spectroscopy, sensitive to local chemical environments, is one of the most powerful tools for studying the crystallization/reaction with nondestructive nature, and can be used to determine the structures and dynamics of solids, liquids, gases, and heterogeneous mixtures at the atomic level.[8-22] Compared with conventional NMR, *in situ* NMR allows the identification of reaction intermediates that could not be found under *ex-situ* conditions. Besides, *in situ* MAS NMR techniques enable us to monitor chemical reactions under real reaction conditions qualitatively and quantitatively, and thus can be utilized to study reaction kinetics, which is helpful to discriminate the reaction intermediates and spectators.[8,15,23-28] However, to obtain high-resolution NMR spectra in solids, the sample loaded in specially designed containers (e.g. rotor) is required to rotate at extremely high speed (several thousand Hz) and at a magic angle (54.74º to the external magnetic field), i.e. MAS NMR technique,[29] to average anisotropic interactions arising from chemical shift anisotropy, dipole-dipole interactions, and quadrupolar interactions. Moreover, as the low sensitivity for commonly observed ^{13}C, ^{29}Si nuclei etc., the sample

volume should be designed as sufficiently large as possible. These requirements bring great challenges for developing *in situ* MAS NMR techniques, in particular high-temperature high-pressure (HTHP) MAS NMR technique, working in very strong magnetic fields up to several Teslas (ca. 7.0 to 18.8 T), because the *in situ* MAS NMR rotors must be a sealable nonmagnetic vessel with high mechanical strength, strong chemical endurance, and maximum sample volumes (Figure 1).[30-31] These technical challenges have been gradually tackled recently by elegant design of the *in situ* MAS NMR rotors and high precision machining techniques, which enables the detecting of material synthesis/ chemical reactions across a wide range of temperatures and pressures.

In this review, we will introduce several traditional *in situ* solid-state MAS NMR techniques briefly, then describe the recent developments of HTHP *in situ* MAS NMR technologies. Finally, the examples of recent applications in material synthesis and heterogeneous catalysis will be represented to manifest the unique features of HTHP *in situ* MAS NMR technique.

n *IN SITU* SOLID-STATE MAS NMR APPROACHES

In situ solid-state MAS NMR techniques allow for recording spectra during the processes of chemical reactions and crystallizations carried out in an *in situ* NMR rotor under controlled atmospheres and temperatures, which are heated inside NMR probes in a wide temperature range from 273 K up to 973 K. They could provide structure and quantitative information on the evolution of reactants, intermediates, products, and also host-guest interactions.[32] In general, two types of *in situ* MAS NMR cells were designed for ambient pressure continuous flow and high pressure batch reactions.

Continuous Flow Conditions. The design of modified MAS

Many reactions are operated **at elevated temperatures and pressures**

| Nonmagnetic vessel with high mechanical strength and strong chemical resistance | Spin several thousand of cycles per second | Seal samples at high temperatures and high pressures |

HTHP *in situ* MAS NMR rotors

Figure 1. Technical complications for the development of *in situ* MAS NMR technique

NMR rotor as continuous flow micro-reactor proposed by Hunger and co-workers is shown in Figure 2, which is utilized to mimic the reaction conditions of a fixed-bed reactor.[33-34] In this design, the solid samples are loaded into a hollow cylinder with a special tool, and an injection tube axially placed at the center of rotor delivers reactants and carrier gas to the bottom of the solid samples. The reactants and carrier gas pass through the solid samples, after which the outflow stream can leave the sample volume *via* an annular gap in the rotor cap and then be analyzed by an on-line gas chromatograph. In addition, this technology can be combined with other characterization techniques, such as UV-Vis spectroscopy by attaching a glass fiber to the stator and housing a quartz window on the bottom of the NMR rotor, which enables us to investigate chemical processes simultaneously by *in situ* MAS NMR, UV-Vis spectroscopy and chromatograph analysis under flow conditions.[35-36]

These *in situ* NMR apparatuses can simulate, to a great extent, the conditions of a real flow catalytic reactors, and have been extensively used for the study of heterogeneous catalysis at ambient pressure.[27-28,32,37-41] Since the micro-reactor is not sealable, this technique is challenged to operate under high-pressure conditions, and also needs a large number of reactants, which may not be economical for isotope-enriched reactants.
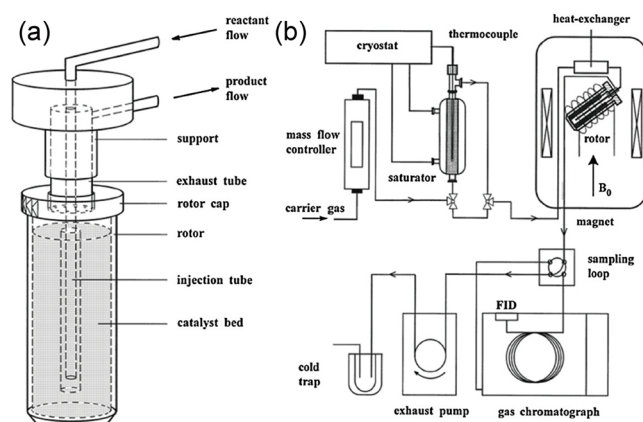
Batch-Like Conditions. The batch-like mode of *in situ* solid-state MAS NMR techniques can overcome the limitations of *in situ* flow MAS NMR, and can be employed to mimic batch autoclave reactors, where many functional materials are hydrothermally or solvothermally synthesized, such as zeolites/MOFs, and many chemical processes like adsorption and reaction take place. The early batch-like *in situ* MAS NMR techniques take the form of flame-sealed glass ampoules (Figure 3) or polymer inserts containing the samples needed to be investigated, which is then placed into a commercial MAS rotor.[42-46] Obviously, the inserts must be highly symmetrical to ensure the stable high spinning rates. Although this method can be used for chemical processes above atmospheric pressure, the quantity of solid samples is quite limited due to the small inner diameters of commercial rotors, and the allowable pressure depends on the material of the inserts. Moreover, it is complicated and dangerous to implement, especially when H_2, CO and other flammable gases are sealed.

Figure 2. Schematic representation of modified MAS NMR rotor micro-reactor (a) for *in situ* flow MAS NMR system (b) with on-line chromatographic. Reprinted with permission from ref.[33] Copyright 1999 Springer-Link.
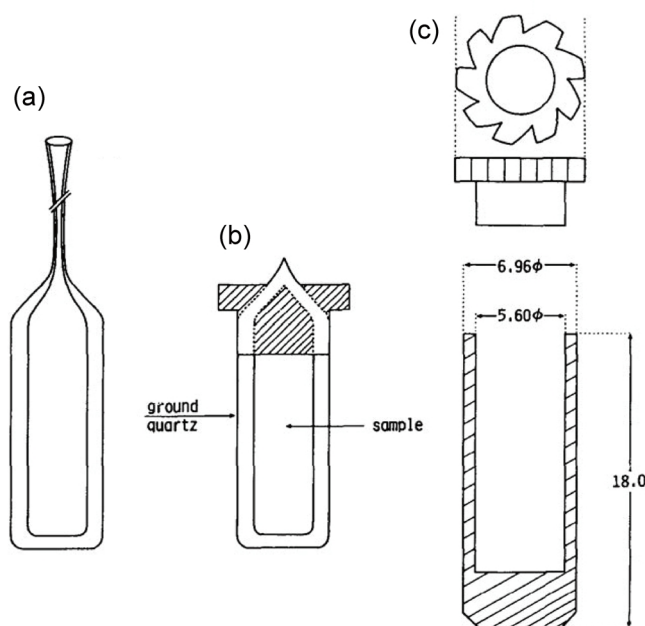

Figure 3. Diagram of flame-sealed glass NMR insert (a and b) incorporating samples and fitting high-speed MAS NMR rotor (c). Reprinted with permission from ref.[42] Copyright 1986 Elsevier Science.
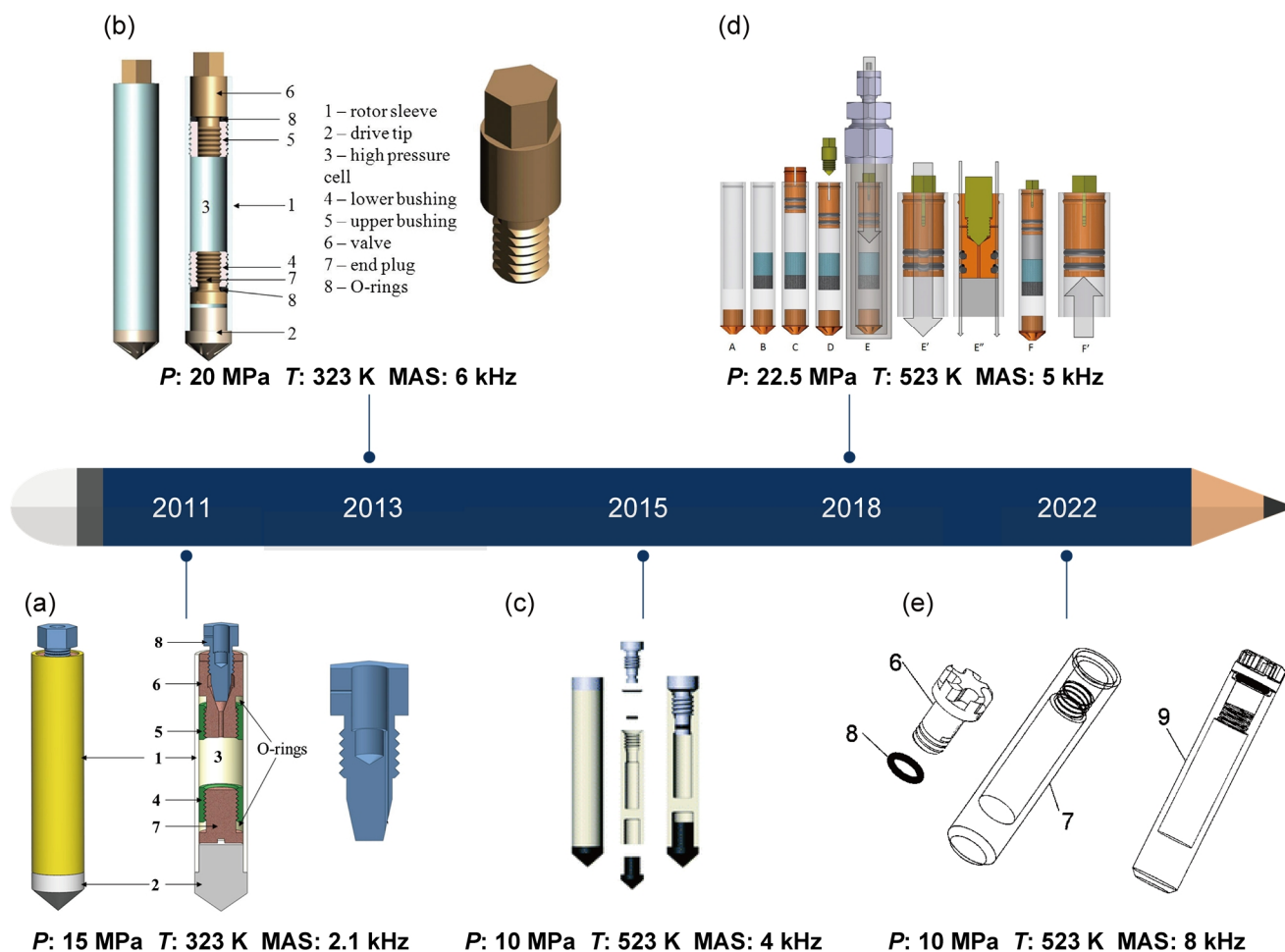
(b)

1 – rotor sleeve
2 – drive tip
3 – high pressure cell
4 – lower bushing
5 – upper bushing
6 – valve
7 – end plug
8 – O-rings

P: 20 MPa T: 323 K MAS: 6 kHz

(d)

P: 22.5 MPa T: 523 K MAS: 5 kHz

2011   2013   2015   2018   2022

(a)

P: 15 MPa T: 323 K MAS: 2.1 kHz

(c)

P: 10 MPa T: 523 K MAS: 4 kHz

(e)

P: 10 MPa T: 523 K MAS: 8 kHz

Figure 4. The development of modern high-temperature high-pressure *in situ* MAS NMR techniques. (a) Reprinted with permission from ref.[47] Copyright 2011 Elsevier Science. (b) Reprinted with permission from ref.[48] Copyright 2013 Elsevier Science. (c) Reprinted with permission from ref.[49] Copyright 2015 The Royal Society of Chemistry. (d) Reprinted with permission from ref.[50] Copyright 2018 American Chemical Society. (e) Reprinted with permission from ref.[51]

n   NEWLY DESIGNED HIGH-PRESSURE *IN SITU* MAS NMR

To solve the problems associated with traditional batch-like *in situ* MAS NMR techniques, Hu and coworkers developed a series of reusable high pressure MAS NMR rotors,[25, 47-49] which are based on commercial rotors with negligible NMR backgrounds. In 2011, they reported the first high-pressure ceramic-based MAS NMR rotor (Figure 4a) and a high-pressure rotor loading chamber was specially designed to seal and re-open the valve of the high-pressure MAS rotor.[47] A modification over a commercially available NMR rotor by abrading the interior surface of the zirconia ceramic cylinder immediately outside the sample space (3) was used for the rotor sleeve (1), and then the plastic bushing (4 and 5) was glued permanently and tightly in place at both ends of the sleeve by using an epoxy, so that removable polymer end plug (7) and valve adapter (6) could be threaded into the bushings with sealing O-rings, and the valve (8) could be mounted to create the desired seal. With this high-pressure MAS NMR rotor, the pressure up to 15 MPa and a sample spinning rate of 2.1 kHz can be achieved.

In this complex design, the plastic valve adaptor (6) was identified as the weakest part of the high pressure rotor, and the use of a large-size rotor with 9.5 mm outside diameter limited the sample spinning rate, which could result in low spectral resolution. Later, Hu and coworkers eliminated the valve adapter, and screwed directly the end plug (7) and valve (6) into the bushings (4 and 5) to press an O-ring (8) to achieve the seal in their modified version in 2013 (Figure 4b).[48] Moreover, because this rotor was fabricated from 7.5 mm MAS rotor sleeve, high-pressure MAS NMR rotor could withstand higher pressure up to 20 MPa while spinning at 6 kHz. These rotors have been applied to study the mineral carbonation reaction for geological carbon sequestration (GCS).[47-48]

Although these designs have been proved successful for high-pressure *in situ* MAS NMR, variable temperature experiments were still limited due to the use of glue and polymer bushing that would expand or shrink during variable temperature operation. In 2014, the authors realized the combination of high-temperature (403 K) and pressure (1 MPa) condition at the MAS rate of 2.4 kHz by using a custom MACOR ceramic (an easily machinable ceramic) insert, which was threaded at the top to enable sealing

with a polymer screw compressing down on a sealing O-ring, which was used for *in situ* investigation of aqueous cyclohexanol dehydration reactions.[25] However, MACOR ceramic is fragile and cannot withstand higher pressure above 10 bar. In 2015, they finally constructed a perfect high-temperature high-pressure *in situ* MAS NMR rotor (Figure 4c),[49] in which the whole body, with the exception of the sealing O-ring and spinning tip, was made of ZrO_2 ceramics by machining a single zirconia rod using diamond grinding tools. The assembly could be used at temperature up to 523 K and pressure exceeding 10 MPa while spinning at 4 kHz. In this design, the top of sleeve was threaded to fit a threaded screw zirconia cap, which included an extruded or socket hexagonal-shaped head for allowing rotation under gas loading chamber to be screwed into the rotor sleeve, where it sealed the sample compartment by compressing the high-temperature sealing O-ring on the O-ring support. In 2018, Walter *et al.* modified the top sealing part, named WHiMS rotor (Figure 4d), employing a one-way-check-valve-like design. This design avoided very challenging machining of thread on ceramic with perfect mass balance by easily machinable plastic parts.[50] However, the use of polymer bushings limited the performances of rotors under high temperature conditions. Subsequently, in 2019, they improved the high-temperature MAS NMR probe by employing simultaneously bearing gas flow and VT gas stream to heat the rotor so as to decrease temperature gradient across the sample rotor. It is beneficial to more precisely control the experimental conditions and enhance the spectrum resolution on account of the more coincident sample NMR properties.[52]

Most of the above designed high pressure rotors are based on pencil-style MAS NMR rotors, suitable for Varian/Agilent/Phoenix probes, which cannot be used on presently widely installed Bruker NMR spectrometers. The Bruker MAS NMR rotors are significantly different from the pencil-style ones. Recently, our group designed a high-temperature high-pressure MAS NMR rotor based on Bruker MAS NMR rotors (Figure 4e). The key of this new design lies in the integration of screw threads on ZrO_2 drive cap of the rotor with very limited length using extremely high precision machining techniques to achieve the high coaxiality required for high speed spinning. The rotor is all made of ZrO_2 ceramic except the sealing O-rings, and can reach a spinning rate above 8 kHz, where the sealing temperature can endure up to 523 K using perfluoroelastomer O-ring and high-pressure up to 10 MPa.[51]

n APPLICATIONS IN MATERIAL SYNTHESIS

Molecular sieves, represented by microporous aluminophosphate materials and zeolites, are a class of important inorganic microporous crystalline materials, and have been extensively applied in the industrial fields of adsorption, separation, ion exchange and catalysis, due to their large surface areas, well-defined and tunable pore structures, strong acidity, along with their ability to incorporate a variety of cations.[53-54] The atomic-level understanding of hydrothermal crystallization process is of great importance for rational engineering tunable synthesis of molecular sieve materials to meet the specific applications. *In situ* MAS NMR is one of the most powerful and informative methods to study the nucleation, crystal growth and phase transformation of molecular

sieve materials regardless of their crystalline or amorphous phases.[46,53-54] Such applications have been reported for the crys-
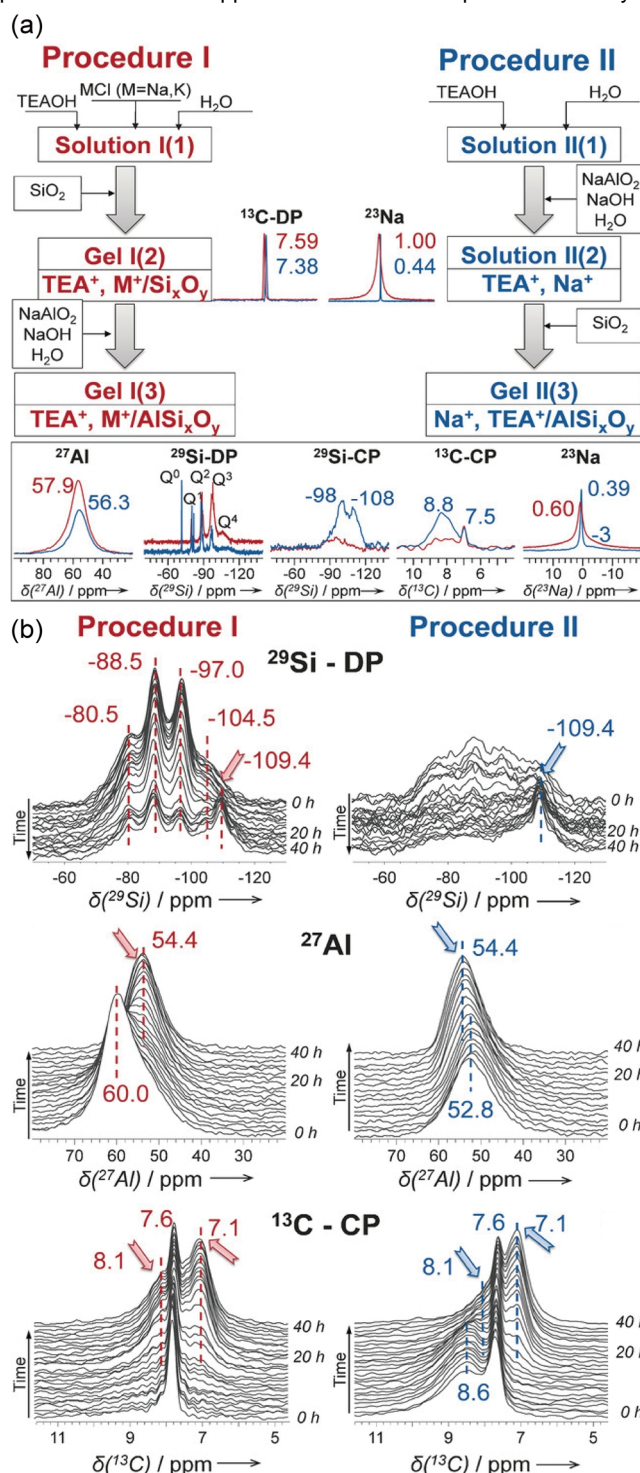
Figure 5. (a) Representation of gel preparation procedures I and II for synthesis of zeolite BEA and the comparison of NMR spectra of the gels. (b) Time-resolved ^{29}Si, ^{27}Al MAS NMR, and ^{13}C CP/MAS NMR of *in situ* monitoring of zeolite BEA formation from the gels prepared according to procedures I and II. Reprinted with permission from ref.[46] Copyright 2017 John Wiley & Sons.

tallization process of $AlPO_4$-5 and subsequent water assisted phase transformation process through the post-treatment. $AlPO_4$-5 molecular sieve synthesized in the *in situ* MAS NMR rotor well reproduces the result in the standard autoclave evidenced by the same characteristic XRD patterns.[49,53-54] The results of *in situ* ^1H, ^{13}C, ^{27}Al and ^{31}P MAS and ^{13}C CP/MAS NMR acquired on $AlPO_4$-5 synthesis process demonstrate a damped oscillating crystallization process, where activated water catalyzes the continuous rearrangement of the local structure of amorphous precursor through repeated hydrolysis and condensation reactions and expulsion of the excess water, phosphate, and aluminums to form a crystalline $AlPO_4$-5.[53] Combined with XRD and SEM, subsequent water assisted phase transform process from $AlPO_4$-5 to thermodynamically more stable dense phase $AlPO_4$-tridymite was also revealed by *in situ* multinuclear MAS NMR, where water first activates the residue amorphous aluminophosphate in isolated crystalline $AlPO_4$-5 sample via hydrolysis and condensation reactions,

and then they will reassemble into $AlPO_4$-tridymite, and the mass transportation from $AlPO_4$-5 to $AlPO_4$-tridymite is established via gradual amorphization of $AlPO_4$-5.[54]

Zeolite BEA is an excellent catalyst for a broad range of industrial processes, and can be synthesized by different procedures with solution-mediated transformation or solid-solid hydrogel rearrangement mechanisms proposed by previous studies.[55-57] Ivanova *et al.* utilized time-resolved *in situ* ^{13}C, ^{27}Al, and ^{29}Si MAS NMR (Figure 5) to monitor the hydrothermal process of zeolite BEA, which was synthesized by different procedures (I and II), to obtain insight into the crystallization mechanism.[46] As shown in Figure 5a, in procedure I, the addition of Si source at the initial step results in formation of the initial gel containing Al-rich $M^+/AlSi_xO_y$, while TEA^+ cations remain in solution, which is confirmed by narrow ^{13}C NMR signal and a broad ^{23}Na resonance line. However, in procedure II, adding Si source at the later step of mixing precursors leads to the formation of TEA^+-containing $AlSi_xO_y$, which is evidenced by the appearance of broad ^{13}C CP/MAS NMR signal at about 8.8 ppm and ^{29}Si CP/MAS NMR. During the hydrothermal crystallization process (Figure 5b), in procedure I, the BEA zeolite is crystallized from solution species, as is clearly evidenced by ^{29}Si MAS NMR, where the signals of Q_1 (-80.5 ppm), Q_2 (-88.5 ppm), Q_3 (-97.0 ppm), and Q_4 (-104.5 ppm) species are well-resolved, indicating the fast exchange between the solid and liquid phases. These ^{29}Si signals disappear gradually at the increase of the new signal at -109.4 ppm corresponding to BEA zeolite, whereas, in procedure II, as is demonstrated by ^{29}Si MAS NMR, heating the gel leads to the formation of solid amorphous hydrogel, which crystallizes into zeolite BEA through solid-solid transformation. The ^{13}C CP/MAS NMR spectra illustrate that, in this procedure, parts of TEA^+ cations are incorporated in solid amorphous gel from the very beginning of hydrothermal crystallization, which is confirmed by the appearance of the signal at about 8.6 ppm attributed from the rigid species involved in solid-state interactions. In contrast, in procedure I, TEA^+ cations remain in solution. The kinetic curves of BEA zeolite crystallization based on these spectra also show that solid-solid transformation results in shorter induction period.[46]

^{23}Na is another sensitive nucleus to monitor the zeolite synthesis due to its fast relaxation time and 100% natural abundance, and Na^+ could play a crucial role of structure-directing agent.[58-60] However, only one slightly asymmetric peak can be observed in the *in situ* ^{23}Na MAS NMR spectra during crystallization of FAU zeolite as the typical quadrupolar line shapes are suppressed by the symmetric hydration sphere.[7] Fortunately, their spinning sidebands exhibit two distinct resonances at -20 ppm arising from the framework sodalite cage and -22 ppm corresponding to the FAU supercage from their isotropic chemical shifts at 2.8 and 0.8 ppm, respectively, which allows to follow the evolution of the structure during the crystallization of zeolite (Figure 6a). Both peak intensities increase gradually as the zeolite is formed (Figure 6b), and one can find that the maximum yield of sodalite units is obtained prior to that of the supercage. In the meantime, the rate of formation of the supercage increases once a threshold concentration of sodalite units is achieved, thus implying that the generation of sodalite units could provide necessary subunites for the con-
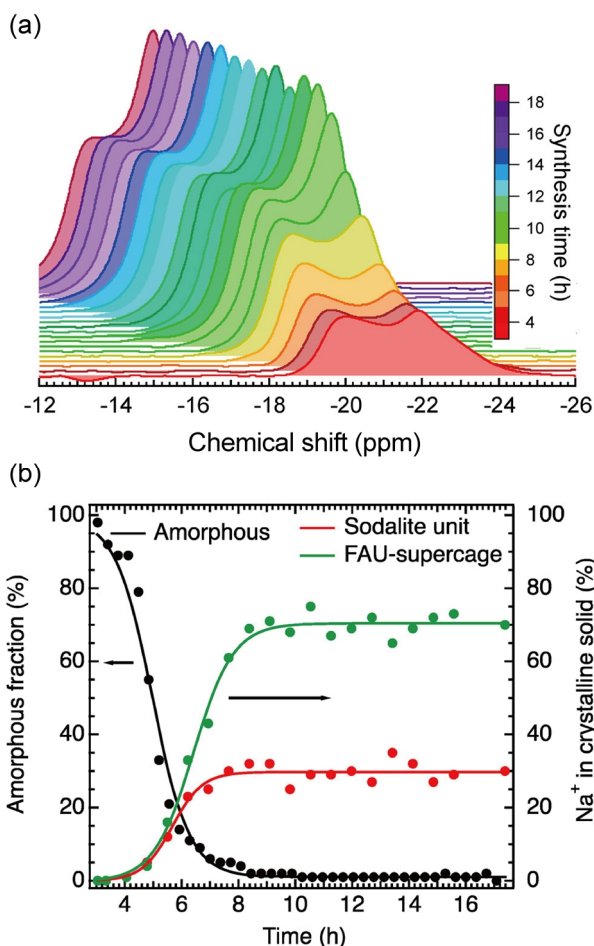
Figure 6. (a) Changes in the spinning side band of *in situ* ^{23}Na MAS NMR spectra as a function of zeolite FAU synthesis time and (b) the kinetic transformation of amorphous material (detected by ^{27}Al MAS NMR line width) into crystalline zeolite FAU as directed by the speciation of Na^+ ions [plotted as formed fraction of the final concentration of sodalite (-20 ppm) and the supercage (-22 ppm)]. Reprinted with permission from ref.[7] Copyright 2018 American Chemical Society.

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Chin. J. Struct. Chem. **2022**, 41, 2210045-2210055

struction of FAU supercage.

These results show that _in situ_ MAS NMR could serve as a distinct tool for monitoring materials synthesis including zeolites,[61] MOFs,[62] COFs, etc., for the design of novel materials for different applications.

n APPLICATIONS IN HETEROGENEOUS CATALYSIS

Traditional _in situ/quasi-in situ_ solid-state MAS NMR approaches have been utilized to study heterogeneous catalysis, including the identification of reaction intermediates and catalytic active sites, determination of catalytic pathways and host-guest interactions, and elucidation of reaction kinetics and catalytic mechanisms.[8,24,31-32,38-39] Most of these studies were carried out at ambient pressure, and those techniques are not applicable to reactions proceeding under high pressure condition. Here, we will show that the HTHP _in situ_ MAS NMR technique has been used to mimic batch autoclave following the catalytic reactions, where the obtained turnover frequency (TOF) and corresponding activation energy are comparable with batch reactions.[49] Moreover, by using isotope selectively labeled substrates, catalysts, or reaction intermediates, the reaction mechanism can be clearly elucidated.[25-26,50,52,63-65]

The hydrodeoxygenation (HDO) of renewable lignin-derived phenolic compounds requires an acid catalyst to catalyze dehydration of the intermediately formed cycloalkanols.[66-67] 1-^{13}C-cy-

(a)

(b)

Figure 7. Stacked plot of the _in situ_ ^{13}C MAS NMR spectrum (a) and proposed reaction pathway (b) of 1-^{13}C-cyclohexanol reacting at 130 °C in liquid water on zeolite HBEA. Reprinted with permission from ref.[25] Copyright 2014 John Wiley & Sons.

clohexanol dehydration in water solvent over zeolite HBEA catalyst at 130 °C was studied using _in situ_ ^{13}C MAS NMR (Figure 7a).[25] In the initial reaction phase, the narrow peak observed at 70 ppm and relatively broad signal at 70.8 ppm are assigned to 1-^{13}C-cyclohexanol in the aqueous phase and 1-^{13}C-cyclohexanol interacting with zeolite, respectively. The area ratio of those two peaks suggests that about 50% of the cyclohexanol is initially adsorbed in the pores of zeolite HBEA, which exemplifies the potential of HTHP _in situ_ MAS NMR to quantify the distribution between the adsorbed and the mobile phase at elevated pressures and temperatures. During the reaction process, the evolution of the signals of cyclohexene and dicyclohexyl ether are monitored by _in situ_ ^{13}C MAS NMR, and at the same time, significant migration of the hydroxyl group in cyclohexanol and the double bond in cyclohexene with respect to the ^{13}C label were observed. Based on the variations in isotope concentrations during catalytic reaction process and reaction kinetic analysis, a reaction pathway was proposed and shown in Figure 7b. The E1-type mechanism fully accounts for the dehydration of cyclohexanol forming a cyclohexyl carbonium ion, which undergoes a 1,2-hydride shift competing with rehydration and deprotonation. Therefore, scrambling of the ^{13}C label in the alicyclic ring was observed. The cyclohexyl oxonium ion can react with another cyclohexanol, forming dicyclohexyl ether, and electrophilic attack of cyclohexene by a cyclohexyl carbenium ion leads to C-C coupling as well as the formation of cyclohexyl-1-cyclohexene.[25]

Alkylation of phenols is an important model reaction for catalytic conversion lignin-derived compounds to value-added chemicals and fuels.[68-72] It is an electrophilic aromatic substitution reaction, which can take place with either alcohols or olefins as alkylating agents. The hypothesized mechanisms for phenol alkylation catalyzed by solid acid catalyst are largely based on mechanistic analogues adapted from classical homogeneous Friedel-Crafts alkylation, especially for alcohol alkylating agent. To clarify the reaction mechanism, HTHP _in situ_ MAS NMR was employed to study phenol alkylation with cyclohexanol and cyclohexene in decalin solvent catalyzed by zeolite HBEA.[64] Time on stream concentrations of reactants, reaction intermediates, and products (Figure 8a-8d) were determined by _in situ_ ^{13}C MAS NMR of the 1-^{13}C-phenol alkylation with 1-^{13}C-cyclohexanol in decalin over zeolite HBEA. The dehydration of cyclohexanol to cyclohexene is the primary transformation during the first 400 min of the reaction, and phenol alkylation does not take place until most of cyclohexanol is consumed, which implies that alkylation reaction was hindered by cyclohexanol. As phenol and cyclohexanol have similar adsorption propensities in the pores of zeolite HBEA, which is evidenced by phenol and cyclohexanol variable temperature adsorption experiments,[64] it can be inferred that the lack of phenol alkylation at the early stage is due to the absence of reactive electrophilic intermediate, which is hardly produced at the early stage of cyclohexanol dehydration. In contrast, when using cyclohexene as an alkylating agent, alkylation transformation happens immediately (Figure 8e). When cyclohexanol is initially added together with cyclohexene, the alkylation transformation is severely retarded again and becomes faster after a significant fraction of cyclohexanol is consumed (Figure 8f), which means that the pre-
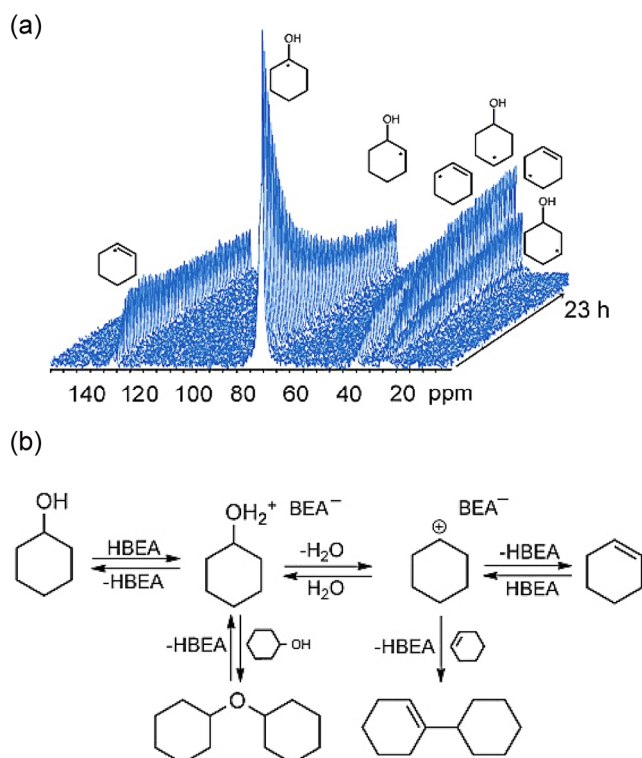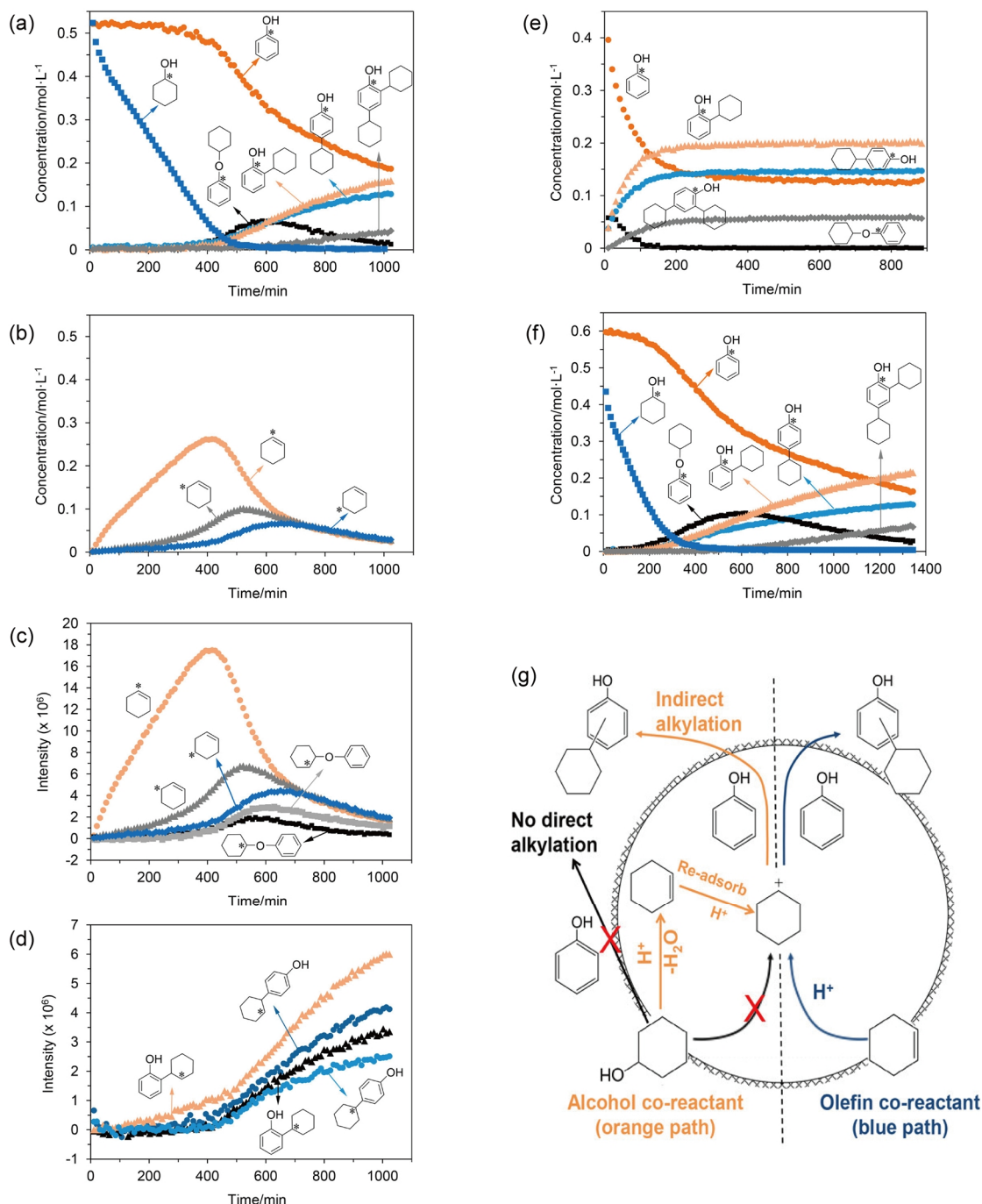
Figure 8. Concentration-time profiles of compounds during the *in situ* ^{13}C NMR investigations of the alkylation of 1-^{13}C-phenol catalyzed by zeolite HBEA with 1-^{13}C-cyclohexanol (a-d), cyclohexene (unlabeled) (e) and with equimolar cyclohexene and 1-^{13}C-cyclohexanol (f) in decalin at 126 °C, and proposed phenol alkylation reaction pathways (g). Reprinted with permission from ref.[64] Copyright 2017 American Chemical Society.

sence of a great number of cyclohexanols inhibits cyclohexene to form the direct alkylating electrophilic intermediate.

Further *in situ* ^{13}C MAS NMR study of 1-^{13}C-cyclohexanol dehydration in decalin over zeolite HBEA showed a negligible extent of ^{13}C label scrambling at the initial reaction stage (Figure 9), which is significantly different from cyclohexanol dehydration in water.[25-26] However, ^{13}C scrambling rate increased significantly

after a major fraction of 1-^{13}C-cyclohexanol is consumed. Based on these observations, combined with the detailed results of the reaction,[26] a scheme about cyclohexanol dehydration via cyclohexanol monomer and dimer pathways was proposed, in which during cyclohexanol-dimer-mediated dehydration stage, the re-adsorption of cyclohexene at the Brønsted acid sites (BAS) yields carbenium ions, which, if present, are at a very low concentration
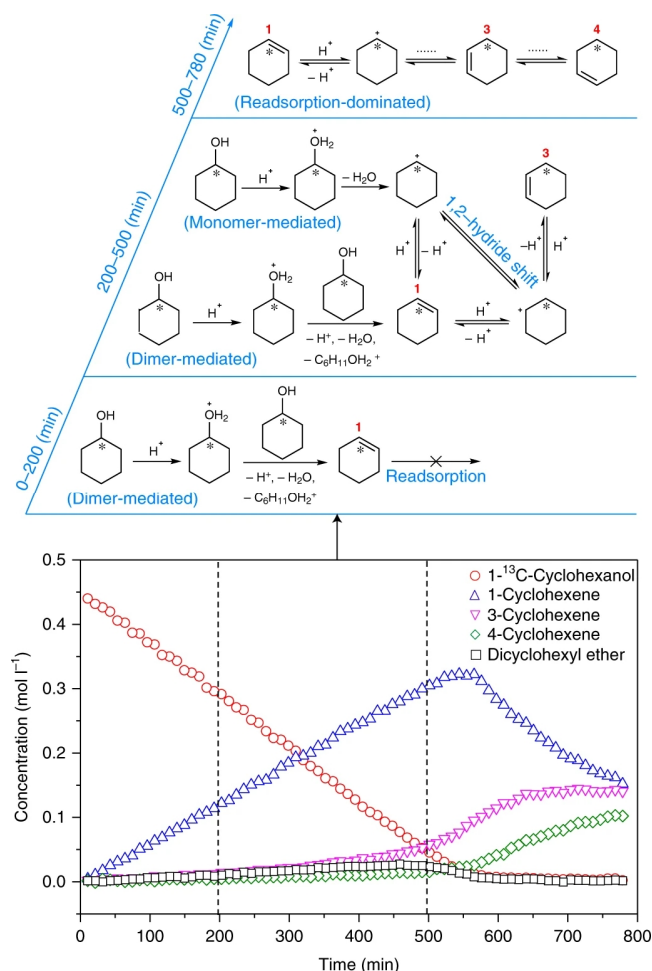
Figure 9. The reaction pathway proposed on the basis of operando ^{13}C NMR measurements of 1-^{13}C-cyclohexanol dehydration at 126 °C in decalin on zeolite HBEA. Reprinted with permission from ref.[26] Copyright 2018 Springer.

For material synthesis, the atomic-level local structures such as the atomic connectivity, coordination status, spatial host-guest interaction, as well as the structural evolution can be quantitatively monitored by _in situ_ MAS NMR regardless of their gas/liquid/solid, amorphous/crystalline phases. For catalytic reactions, the structures of reaction intermediates, reaction kinetics, combined with control isotope experiments, and the reaction pathways can be clearly elucidated by _in situ_ MAS NMR. More applications have been expected, with the development of modern HTHP _in situ_ MAS NMR techniques and advanced NMR pulse sequences, including the exploration of interactions between reactants and catalysts, elucidation of reaction mechanisms and investigation of reaction kinetics under reaction conditions at high pressure and temperature. Furthermore, on the aspect of technical development, _in situ_ MAS NMR still needs several breakthroughs, including faster spinning rate, tolerance of harsher conditions (temperature, pressure), faster heating up, etc. In addition, high magnetic fields benefiting NMR sensitivity and resolution, as well as the specially designed NMR pulse sequences for dipolar or chemical shift anisotropy (CSA) recoupling, sensitivity enhancement and ultrafast 2D NMR, are always helpful in resolving key molecular-level questions of more challenging systems. Finally, the high-temperature high-pressure operando MAS NMR under flow conditions is another big challenge, in which the very creative designs of NMR sample micro-reactor and special NMR probe will be highly demanded.

n ACKNOWLEDGEMENTS

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n COMPETING INTERESTS

The authors declare no competing interests.

n ADDITIONAL INFORMATION

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n REFERENCES

(1) Weckhuysen, B. M. Preface: recent advances in the _in-situ_ characterization of heterogeneous catalysts. _Chem. Soc. Rev._ **2010**, 39, 4557-4559.

(2) Fan, F. T.; Feng, Z. C.; Li, C. UV Raman spectroscopic study on the synthesis mechanism and assembly of molecular sieves. _Chem. Soc. Rev._ **2010**, 39, 4794-4801.

(3) Lamberti, C.; Zecchina, A.; Groppo, E.; Bordiga, S. Probing the surfaces of heterogeneous catalysts by _in situ_ IR spectroscopy. _Chem. Soc._

and will be drastically hindered by alcohol dimer species. As the cyclohexanol is gradually converted, the dehydration transformation shifts to the monomer-mediated pathway where the cyclohexyl carbenium ion is involved, and the cyclohexene can be re-adsorbed and protonated. Carbenium ions are identified as direct alkylating electrophilic agent, and consequently, the clear reaction mechanism of solid-acid-catalyzed phenol alkylation in the apolar solvent decalin can be proposed (Figure 8g), and the ability of solvent on the determination of reaction pathway is identified.[64]

n SUMMARY AND OUTLOOK

The broad applications of solid state MAS NMR techniques promote the development of _in situ_ MAS NMR for practical applications from ambient pressure to above 10 MPa with significantly improved sample volumes. The _in situ_ MAS NMR techniques can be divided into batch and continuous flow condition for practical applications. For batch condition, the _in situ_ techniques have been developed from glass/plastic insert to ceramic insert and from modification of commercial rotors to recently redesigned threaded rotors for applications in much higher pressures and temperatures.

Rev. **2010**, 39, 4951-5001.

(4) Yao, S.; Zhang, X.; Zhou, W.; Gao, R.; Xu, W.; Ye, Y.; Lin, L.; Wen, X.; Liu, P.; Chen, B.; Crumlin, E.; Guo, J.; Zuo, Z.; Li, W.; Xie, J.; Lu, L.; Kiely, C. J.; Gu, L.; Shi, C.; Rodriguez, J. A.; Ma, D. Atomic-layered Au clusters on α-MoC as catalysts for the low-temperature water-gas shift reaction. *Science* **2017**, 357, 389.

(5) O'Brien, M. G.; Beale, A. M.; Weckhuysen, B. M. The role of synchrotron radiation in examining the self-assembly of crystalline nanoporous framework materials: from zeolites and aluminophosphates to metal organic hybrids. *Chem. Soc. Rev.* **2010**, 39, 4767-4782.

(6) Su, D. S.; Zhang, B.; Schlögl, R. Electron microscopy of solid catalysts-transforming from a challenge to a toolbox. *Chem. Rev.* **2015**, 115, 2818-2882.

(7) Prodinger, S.; Vjunov, A.; Hu, J. Z.; Fulton, J. L.; Camaioni, D. M.; Derewinski, M. A.; Lercher, J. A. Elementary steps of faujasite formation followed by *in situ* spectroscopy. *Chem. Mater.* **2018**, 30, 888-897.

(8) Zhang, W.; Xu, S.; Han, X.; Bao, X. *In situ* solid-state NMR for heterogeneous catalysis: a joint experimental and theoretical approach. *Chem. Soc. Rev.* **2012**, 41, 192-210.

(9) Liang, L.; Ji, Y.; Chen, K.; Gao, P.; Zhao, Z.; Hou, G. Solid-state NMR dipolar and chemical shift anisotropy recoupling techniques for structural and dynamical studies in biological systems. *Chem. Rev.* **2022**, 122, 9880-9942.

(10) Du, J.-H.; Chen, L.; Zhang, B.; Chen, K.; Wang, M.; Wang, Y.; Hung, I.; Gan, Z.; Wu, X.-P.; Gong, X.-Q.; Peng, L. Identification of CO_2 adsorption sites on MgO nanosheets by solid-state nuclear magnetic resonance spectroscopy. *Nat. Commun.* **2022**, 13, 707.

(11) Madsen, R. S. K.; Qiao, A.; Sen, J.; Hung, I.; Chen, K.; Gan, Z.; Sen, S.; Yue, Y. Ultrahigh-field ^{67}Zn NMR reveals short-range disorder in zeolitic imidazolate framework glasses. *Science* **2020**, 367, 1473.

(12) Reif, B.; Ashbrook, S. E.; Emsley, L.; Hong, M. Solid-state NMR spectroscopy. *Nat. Rev. Methods Primers* **2021**, 1, 2.

(13) Marchetti, A.; Chen, J.; Pang, Z.; Li, S.; Ling, D.; Deng, F.; Kong, X. Understanding surface and interfacial chemistry in functional nano-materials *via* solid-state NMR. *Adv. Mater.* **2017**, 29, 1605895.

(14) Zheng, A.; Li, S.; Liu, S.-B.; Deng, F. Acidic properties and structure-activity correlations of solid acid catalysts revealed by solid-state NMR spectroscopy. *Acc. Chem. Res.* **2016**, 49, 655-663.

(15) Jaegers, N. R.; Mueller, K. T.; Wang, Y.; Hu, J. Z. Variable temperature and pressure operando MAS NMR for catalysis science and related materials. *Acc. Chem. Res.* **2020**, 53, 611-619.

(16) Peng, Y.-K.; Tsang, S.-C. E. Probe-assisted NMR: recent progress on the surface study of crystalline metal oxides with various terminated facets. *Magn. Reson. Lett.* **2022**, 2, 9-16.

(17) Xia, Y.; Xia, C.; Yi, X.; Liu, F.; Liu, S.; Zheng, A. Progress in the studies on Sn-zeolites by solid state nuclear magnetic resonance. *Chin. J. Magn. Reson.* **2021**, 38, 571-584.

(18) Hu, H.; Wang, W.; Xu, J.; Deng, F. 1,3-Butadienen hydrogenation on supported Pd-Sn bimetallic catalysts investigated by parahydrogen induced polarization. *Chin. J. Magn. Reson.* **2022**, 39, 133-143.

(19) Ji, Y.; Gao, P.; Zhao, Z.; Xiao, D.; Han, Q.; Chen, H.; Gong, K.; Chen, K.; Han, X.; Bao, X.; Hou, G. Oxygenate-based routes regulate syngas conversion over oxide-zeolite bifunctional catalysts. *Nat. Catal.* **2022**, 5, 594-604.

(20) Chen, Y.; Gong, K.; Jiao, F.; Pan, X.; Hou, G.; Si, R.; Bao, X. C-C bond formation in syngas conversion over zinc sites grafted on ZSM-5 zeolite.

Angew. Chem. Int. Ed. **2020**, 59, 6529-6534.

(21) Chen, X.; Fu, Y.; Yue, B.; He, H. Acidity and basicity of solid acid catalysts studied by solid-state NMR. *Chin. J. Magn. Reson.* **2021**, 38, 491-502.

(22) Zhao, Z.; Xiao, D.; Chen, K.; Wang, R.; Liang, L.; Liu, Z.; Hung, I.; Gan, Z.; Hou, G. Nature of five-coordinated Al in γ-Al_2O_3 revealed by ultra-high-field solid-state NMR. *ACS Cent. Sci.* **2022**, 8, 795-803.

(23) Xu, S.; Zhang, W.; Liu, X.; Han, X.; Bao, X. Enhanced *in situ* continuous-flow MAS NMR for reaction kinetics in the nanocages. *J. Am. Chem. Soc.* **2009**, 131, 13722-13727.

(24) Ivanova, II; Kolyagin, Y. G. Impact of *in situ* MAS NMR techniques to the understanding of the mechanisms of zeolite catalyzed reactions. *Chem. Soc. Rev.* **2010**, 39, 5018-5050.

(25) Vjunov, A.; Hu, M. Y.; Feng, J.; Camaioni, D. M.; Mei, D.; Hu, J. Z.; Zhao, C.; Lercher, J. A. Following solid-acid-catalyzed reactions by MAS NMR spectroscopy in liquid phase—zeolite-catalyzed conversion of cyclohexanol in water. *Angew. Chem. Int. Ed.* **2014**, 53, 479-482.

(26) Liu, Y.; Baráth, E.; Shi, H.; Hu, J.; Camaioni, D. M.; Lercher, J. A. Solvent-determined mechanistic pathways in zeolite-H-BEA-catalysed phenol alkylation. *Nat. Catal.* **2018**, 1, 141-147.

(27) Gao, S.; Xu, S.; Wei, Y.; Liu, Z. Applications of solid-state nuclear magnetic resonancespectroscopy in methanol-to-olefins reaction. *Chin. J. Magn. Reson.* **2021**, 38, 433-447.

(28) Zeng, S.; Xu, S.; Wei, Y.; Liu, Z. Investigation of the ethanol dehydration to ethene reaction on H-SSZ-13 Molecular Sieve by *in situ* solid-state NMR spectroscopy. *Chin. J. Magn. Reson.* **2022**, 39, 123-132.

(29) Andrew, E. R.; Bradbury, A.; Eades, R. G. Nuclear magnetic resonance spectra from a crystal rotated at high speed. *Nature* **1958**, 182, 1659.

(30) Jaegers, N. R.; Hu, M. Y.; Hoyt, D. W.; Wang, Y.; Hu, J. Z. Development and application of *in situ* high-temperature, high-pressure magic angle spinning NMR. *In Modern Magnetic Resonance*. Webb, G. A., Ed. Springer International Publishing: Cham **2017**, pp 1-19.

(31) Zhang, L.; Ren, Y. H.; Yue, B.; He, H. Y. Recent development in *in situ* NMR study on heterogeneous catalysis: mechanisms of light alkane functionalisation. *Chem. Commun.* **2012**, 48, 2370-2384.

(32) Blasco, T. Insights into reaction mechanisms in heterogeneous catalysis revealed by *in situ* NMR spectroscopy. *Chem. Soc. Rev.* **2010**, 39, 4685-4702.

(33) Hunger, M.; Seiler, M.; Horvath, T. A technique for simultaneous *in situ* MAS NMR and on-line gas chromatographic studies of hydrocarbon conversions on solid catalysts under flow conditions. *Catal. Lett.* **1999**, 57, 199-204.

(34) Hunger, M.; Horvath, T. A new MAS NMR probe for *in situ* investigations of hydrocarbon conversion on solid catalysts under continuous-flow conditions. *J. Chem. Soc., Chem. Commun.* **1995**, 1423-1424.

(35) Hunger, M.; Wang, W. Formation of cyclic compounds and carbenium ions by conversion of methanol on weakly dealuminated zeolite H-ZSM-5 investigated via a novel *in situ* CF MAS NMR/UV-Vis technique. *Chem. Commun.* **2004**, 584-585.

(36) Wang, W.; Jiang, Y.; Hunger, M. Mechanistic investigations of the methanol-to-olefin (MTO) process on acidic zeolite catalysts by *in situ* solid-state NMR spectroscopy. *Catal. Today* **2006**, 113, 102-114.

(37) Hunger, M. *In situ* NMR spectroscopy in heterogeneous catalysis. *Catal. Today* **2004**, 97, 3-12.

(38) Hunger, M. *In situ* flow MAS NMR spectroscopy: state of the art and applications in heterogeneous catalysis. *Prog. Nucl. Magn. Reson. Spectrosc.* **2008**, 53, 105-127.

(39) Xu, J.; Wang, Q.; Li, S.; Deng, F. *In situ* solid-state NMR investigation of catalytic reactions on zeolites. *In Solid-State NMR in Zeolite Catalysis.* Xu, J.; Wang, Q.; Li, S.; Deng, F., Eds. Springer Singapore: Singapore **2019**, pp 199-254.

(40) He, T.; Ren, P.; Liu, X.; Xu, S.; Han, X.; Bao, X. Direct observation of DME carbonylation in the different channels of H-MOR zeolite by continuous-flow solid-state NMR spectroscopy. *Chem. Commun.* **2015**, 51, 16868-16870.

(41) Hu, J. Z.; Sears, J. A.; Mehta, H. S.; Ford, J. J.; Kwak, J. H.; Zhu, K.; Wang, Y.; Liu, J.; Hoyt, D. W.; Peden, C. H. A large sample volume magic angle spinning nuclear magnetic resonance probe for *in situ* investigations with constant flow of reactants. *Phys. Chem. Chem. Phys.* **2012**, 14, 2137-2143.

(42) Adrian Carpenter, T.; Klinowski, J.; Tilak, D.; Tennakoon, B.; Smith, C. J.; Edwards, D. C. Sealed capsules for convenient acquisition of variable-temperature controlled-atmosphere magic-angle-spinning NMR spectra of solids. *J. Magn. Reson.* **1986**, 68, 561-563.

(43) Anderson, M. W.; Klinowski, J. Direct observation of shape selectivity in zeolite ZSM-5 by magic-angle-spinning NMR. *Nature* **1989**, 339, 200-203.

(44) Deuchande, T.; Breton, O.; Haedelt, J.; Hughes, E. Design and performance of a high pressure insert for use in a standard magic angle spinning NMR probe. *J. Magn. Reson.* **2006**, 183, 178-182.

(45) Yonker, C. R.; Linehan, J. C. The use of supercritical fluids as solvents for NMR spectroscopy. *Prog. Nucl. Mag. Res. Sp.* **2005**, 47, 95-109.

(46) Ivanova, I. I.; Kolyagin, Y. G.; Kasyanov, I. A.; Yakimov, A. V.; Bok, T. O.; Zarubin, D. N. Time-resolved *in situ* MAS NMR monitoring of the nucleation and growth of zeolite BEA catalysts under hydrothermal conditions. *Angew. Chem. Int. Ed.* **2017**, 56, 15344-15347.

(47) Hoyt, D. W.; Turcu, R. V.; Sears, J. A.; Rosso, K. M.; Burton, S. D.; Felmy, A. R.; Hu, J. Z. High-pressure magic angle spinning nuclear magnetic resonance. *J. Magn. Reson.* **2011**, 212, 378-385.

(48) Turcu, R. V.; Hoyt, D. W.; Rosso, K. M.; Sears, J. A.; Loring, J. S.; Felmy, A. R.; Hu, J. Z. Rotor design for high pressure magic angle spinning nuclear magnetic resonance. *J. Magn. Reson.* **2013**, 226, 64-69.

(49) Hu, J. Z.; Hu, M. Y.; Zhao, Z.; Xu, S.; Vjunov, A.; Shi, H.; Camaioni, D. M.; Peden, C. H.; Lercher, J. A. Sealed rotors for *in situ* high temperature high pressure MAS NMR. *Chem. Commun.* **2015**, 51, 13458-13461.

(50) Walter, E. D.; Qi, L.; Chamas, A.; Mehta, H. S.; Sears, J. A.; Scott, S. L.; Hoyt, D. W. Operando MAS NMR reaction studies at high temperatures and pressures. *J. Phys. Chem. C* **2018**, 122, 8209-8215.

(51) Zhao, Z.; Hou, G.; Liu, X.; Yao, X.; Bao, X. Sealed sample cell for high-temperature high-pressure magic angle spinning nuclear magnetic resonance. CN114235876A, 2022-03-25, **2022**.

(52) Mehta, H. S.; Chen, Y.; Sears, J. A.; Walter, E. D.; Campos, M.; Kothandaraman, J.; Heldebrant, D. J.; Hoyt, D. W.; Mueller, K. T.; Washton, N. M. A novel high-temperature MAS probe with optimized temperature gradient across sample rotor for *in-situ* monitoring of high-temperature high-pressure chemical reactions. *Solid State Nucl. Magn. Reson.* **2019**, 102, 31-35.

(53) Zhao, Z.; Xu, S.; Hu, M. Y.; Bao, X.; Hu, J. Z. *In situ* high temperature high pressure MAS NMR study on the crystallization of AlPO₄-5. *J. Phys. Chem. C* **2016**, 120, 1701-1708.

(54) Xu, S.; Zhao, Z.; Hu, M. Y.; Han, X.; Hu, J. Z.; Bao, X. Investigation of water assisted phase transformation process from AlPO₄-5 to AlPO₄-tridymite. *Microporous Mesoporous Mater.* **2016**, 223, 241-246.

(55) Camblor, M. A.; Mifsud, A.; Pérez-Pariente, J. Influence of the synthesis conditions on the crystallization of zeolite Beta. *Zeolites* **1991**, 11, 792-797.

(56) Nicolle, M. A.; Di Renzo, F.; Fajula, F.; Espiau, P.; Courieres, T. D. A microporous tetraethylammonium permutite as synthesis intermediate of the zeolite beta. *In Proceedings from the Ninth International Zeolite Conference.* von Ballmoos, R.; Higgins, J. B.; Treacy, M. M. J., Eds. Butterworth-Heinemann: **1993**, pp 313-320.

(57) Ikuno, T.; Chaikittisilp, W.; Liu, Z.; Iida, T.; Yanaba, Y.; Yoshikawa, T.; Kohara, S.; Wakihara, T.; Okubo, T. Structure-directing behaviors of tetraethylammonium cations toward zeolite beta revealed by the evolution of aluminosilicate species formed during the crystallization process. *J. Am. Chem. Soc.* **2015**, 137, 14533-14544.

(58) Hu, J. Z.; Zhang, X.; Jaegers, N. R.; Wan, C.; Graham, T. R.; Hu, M.; Pearce, C. I.; Felmy, A. R.; Clark, S. B.; Rosso, K. M. Transitions in Al coordination during gibbsite crystallization using high-field ²⁷Al and ²³Na MAS NMR spectroscopy. *J. Phys. Chem. C* **2017**, 121, 27555-27562.

(59) Wang, Z.; Chu, W.; Zhao, Z.; Liu, Z.; Chen, H.; Xiao, D.; Gong, K.; Li, F.; Li, X.; Hou, G. The role of organic and inorganic structure-directing agents in selective Al substitution of zeolite. *J. Phys. Chem. Lett.* **2021**, 12, 9398-9406.

(60) Feuerstein, M.; Hunger, M.; Engelhardt, G.; Amoureux, J. P. Characterisation of sodium cations in dehydrated zeolite NaX by ²³Na NMR spectroscopy. *Solid State Nucl. Magn. Reson.* **1996**, 7, 95-103.

(61) Ivanova, I. I.; Kolyagin, Y. G. Application of multinuclear MAS NMR for the *in situ* monitoring of hydrothermal synthesis of zeolites. *Chem. Eur. J.* **2021**, 27, 14143-14167.

(62) Jones, C. L.; Hughes, C. E.; Yeung, H. H. M.; Paul, A.; Harris, K. D. M.; Easun, T. L. Exploiting *in situ* NMR to monitor the formation of a metal-organic framework. *Chem. Sci.* **2021**, 12, 1486-1494.

(63) Qi, L.; Alamillo, R.; Elliott, W. A.; Andersen, A.; Hoyt, D. W.; Walter, E. D.; Han, K. S.; Washton, N. M.; Rioux, R. M.; Dumesic, J. A.; Scott, S. L. Operando solid-state NMR observation of solvent-mediated adsorption-reaction of carbohydrates in zeolites. *ACS Catal.* **2017**, 7, 3489-3500.

(64) Zhao, Z.; Shi, H.; Wan, C.; Hu, M. Y.; Liu, Y.; Mei, D.; Camaioni, D. M.; Hu, J. Z.; Lercher, J. A. Mechanism of phenol alkylation in zeolite H-BEA using *in situ* solid-state NMR spectroscopy. *J. Am. Chem. Soc.* **2017**, 139, 9178-9185.

(65) Wang, M.; Jaegers, N. R.; Lee, M.-S.; Wan, C.; Hu, J. Z.; Shi, H.; Mei, D.; Burton, S. D.; Camaioni, D. M.; Gutierrez, O. Y.; Glezakou, V.-A.; Rousseau, R.; Wang, Y.; Lercher, J. A. Genesis and stability of hydronium ions in zeolite channels. *J. Am. Chem. Soc.* **2019**, 141, 3444-3455.

(66) Zhao, C.; Kasakov, S.; He, J.; Lercher, J. A. Comparison of kinetics, activity and stability of Ni/HZSM-5 and Ni/Al₂O₃-HZSM-5 for phenol hydrodeoxygenation. *J. Catal.* **2012**, 296, 12-23.

(67) Zhao, C.; Lercher, J. A. Selective hydrodeoxygenation of lignin-derived phenolic monomers and dimers to cycloalkanes on Pd/C and HZSM-5 catalysts. *ChemCatChem* **2012**, 4, 64-68.

(68) Zakzeski, J.; Bruijnincx, P. C. A.; Jongerius, A. L.; Weckhuysen, B. M. The catalytic valorization of lignin for the production of renewable chemicals. *Chem. Rev.* **2010**, 110, 3552-3599.

(69) Besson, M.; Gallezot, P.; Pinel, C. Conversion of biomass into chemicals over metal catalysts. *Chem. Rev.* **2014**, 114, 1827-1870.

(70) Nie, L.; Resasco, D. E. Improving carbon retention in biomass conversion by alkylation of phenolics with small oxygenates. *Appl. Catal. A: Gen.* **2012**, 447-448, 14-21.

(71) Zhao, C.; Camaioni, D. M.; Lercher, J. A. Selective catalytic hydroalkylation and deoxygenation of substituted phenols to bicyclo-alkanes. *J. Catal.* **2012**, 288, 92-103.

(72) Zhao, C.; Song, W.; Lercher, J. A. Aqueous phase hydroalkylation and hydrodeoxygenation of phenol by dual functional catalysts comprised of Pd/C and H/La-BEA. *ACS Catal.* **2012**, 2, 2714-2723.

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