

Basic Principles and Applications of Solid-State NMR in Catalysis

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Nuclear magnetic resonance, NMR, is a modern spectroscopic technique which has been applied in a diversity of disciplines including chemistry, biochemistry, materials science and geoscience. NMR spectroscopy is primarily concerned with interactions between isolated spin pairs. The NMR Hamiltonian operator for an isolated spin pair in an applied external magnetic field, B_0 , is given by

$$\hat{H}_{\text{NMR}} = \hat{H}_Z + \hat{H}_{\text{CS}} + \hat{H}_D + \hat{H}_J + \hat{H}_Q \quad (1)$$

where \hat{H}_Z represents the Zeeman interaction and \hat{H}_{CS} represents the nuclear magnetic shielding interaction; \hat{H}_D and \hat{H}_J represent the direct dipolar and indirect nuclear spin-spin coupling interactions, respectively. The last term \hat{H}_Q denotes the quadrupolar interaction for quadrupolar nuclei.

All isotopes in periodic table are NMR active nuclei except those with even atomic numbers and even mass numbers (e.g., ^{12}C , ^{16}O , etc.). Isotopes with a nuclear spin quantum number, $I=1/2$, are the most commonly observed nuclei in NMR experiments, including ^1H , ^{13}C , ^{15}N , ^{19}F , ^{29}Si , ^{31}P , $^{107,109}\text{Ag}$, ^{195}Pt and $^{203,205}\text{Tl}$ [1]. Quadrupolar nuclei are those with spin (I) greater than $1/2$, and constitute ca. 70% of NMR active nuclei in the Periodic Table as indicated in Figure 1, such as ^2D ($I=1$), ^7Li ($I=3/2$), ^{11}B ($I=3/2$), ^{17}O ($I=5/2$), ^{23}Na ($I=3/2$), ^{27}Al ($I=5/2$), $^{69,71}\text{Ga}$ ($I=3/2$) and $^{113,115}\text{In}$ ($I=9/2$). From the analysis of the NMR spectrum, useful information such as structural and dynamic information could be determined. The information, arising from different NMR interactions shown in Eq. (1), includes the chemical shift, CS, tensor and the indirect spin-spin coupling constants, J , between coupled nuclei. For quadrupolar nuclei, one also can extract the electric field gradient, EFG, tensors for these nuclei.

Depending on the states of the matter studied, NMR spectroscopy can be mainly classified into two categories: solution and solid-state NMR (SSNMR). Solution NMR generally studies compounds dissolved in low-viscosity solvents and high-resolution NMR spectra can be obtained, which is the main advantage of this technique over SSNMR. The high-resolution NMR spectra in solution arise from the averaging of several NMR interactions due to rapid molecular tumbling. In contrast, the absence of rapid molecular motion for solid samples

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1/2																	1/2
3/2	3/2											3/2	1/2	1	5/2	1/2	3/2
3/2	5/2											5/2	1/2	1/2	3/2	3/2	
3/2	7/2	7/2	5/2	7/2	3/2	5/2	1/2	7/2	3/2	3/2	5/2	3/2	9/2	3/2	1/2	3/2	9/2
5/2	9/2	1/2	5/2	9/2	5/2	9/2	5/2	1/2	5/2	1/2	1/2	9/2	1/2	5/2	1/2	5/2	3/2
7/2	3/2	7/2	7/2	7/2	1/2	5/2	3/2	3/2	1/2	3/2	3/2	1/2	1/2	9/2	1/2		
3/2			3/2														
				7/2		5/2	7/2	5/2	7/2	5/2	3/2	3/2	5/2	7/2	7/2	1/2	5/2
				5/2		3/2	7/2	5/2		5/2							

Figure 1: NMR Periodic Table indicating the spin number of the highest naturally occurring isotope of each element; the blank square refers to $I=0$.

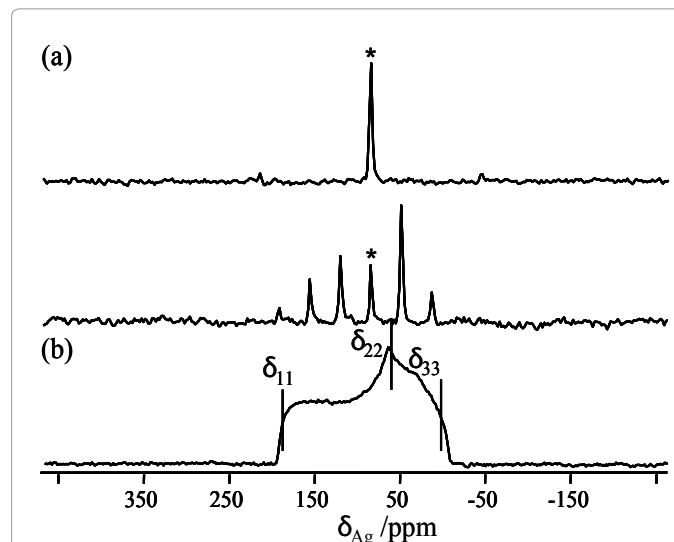


Figure 2: (a) ^{109}Ag CP/MAS NMR spectra of AgSO_3CH_3 at different spinning rates, $v_{\text{rot}} = 830$ Hz (lower trace) and at $v_{\text{rot}} = 3$ kHz (upper trace); the asterisk refers to δ_{iso} and the spikes refer to spinning sidebands. (b) ^{109}Ag NMR spectrum of a stationary sample of AgSO_3CH_3 . (a-b) $B_0 = 11.75$ T [2]. The shift values are referenced to AgNO_3 (1M) ($\delta(^{109}\text{Ag}) = 0$ ppm).

leads to broad peaks in SSNMR spectra that often contain spectral features. However, the development of the magic-angle spinning (MAS) technique allows the spectroscopists to produce “solution-like” NMR spectra of solid samples, from which similar information as from solution NMR can be obtained. Figure 2 shows an example of solid-state ^{109}Ag NMR spectra of AgSO_3CH_3 acquired with cross-polarization (CP) enhancement technique under MAS or stationary conditions [2]. From the analysis of the features in the solid-state ^{109}Ag NMR spectra of MAS and stationary samples, CS tensor including isotropic (δ_{iso}) and anisotropic (δ_{11} , δ_{22} and δ_{33}) chemical shift values can be determined. For quadrupolar nuclei, additional information such as EFG tensor and the relative orientation of CS and EFG tensors can also be determined. There are also several other advantages for SSNMR spectroscopy; for example, it is available to insoluble samples. In addition, many compounds do not maintain their solid-state structure or are unstable when dissolved in a solvent. Thus SSNMR spectroscopy can provide structural and dynamic information unavailable from solution NMR and other techniques such as single-crystal X-ray diffraction (XRD)

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due to the difficulties to grow suitable single crystals for examination by XRD.

In the field of heterogeneous catalysis, SSNMR spectroscopy is a very useful tool for the investigation of framework atoms and extra-framework species including surface sites of solid catalysts, reactants, adsorbate complexes and reaction intermediates formed on these materials. For extra-framework species, many nuclei such as ^1H , ^2D , ^{13}C , ^{15}N , ^{19}F and ^{31}P are NMR active which could be used to study the Brønsted and Lewis acid/base sites of solid catalysts, dynamic information, reaction intermediates and even *in/ex situ* reactions on these catalysts. Herein, we will not discuss these studies in detail and many reviews and textbooks have been published such as refs [3-11] and references therein.

Tetrahedral SiO_4 units in the framework of zeolite catalysts are the basic structural blocks and various metal atoms including Al, B, Ga and Ti can be incorporated to these SiO_4 units. In the case of Al atoms incorporated with SiO_4 units, there are up to five different environments surrounding the tetrahedrally coordinated silicon atoms (Q4), denoted Si(nAl) with $n=0, 1, 2, 3$ and 4 [10]. For each type of Si(nAl) species, a ^{29}Si MAS NMR signal is shown in a well-defined range of chemical shifts, as shown in Figure 3. In addition, the nSi/nAl ratio in the framework of zeolite catalysts can be calculated via Eq. (2) [10]. Similarly, ^{29}Si MAS NMR spectra can provide the framework chemical compositions for the gallium [11] and zinc [12] analogues of zeolite catalysts. Also, useful structural information of zeolite catalysts can be acquired from solid-state ^{17}O and ^{27}Al NMR spectra [8].

$$(\text{Si}/\text{Al})_{\text{NMR}} = \sum_{n=0}^4 I_{\text{Si}(n\text{Al})} / \sum_{n=0}^4 0.25nI_{\text{Si}(n\text{Al})}$$

As briefly described above, SSNMR spectroscopy is a very useful technique for the investigation of local structure, dynamics and reactions on solid catalysts. Nowadays, SSNMR spectroscopy has become a routine method for the characterization of solid catalysts in recent decades due to the development of new techniques and the increase of commercial magnetic field strength. Thus, it would be expected that SSNMR will play more and more important roles for the research in the field of heterogeneous catalysis.

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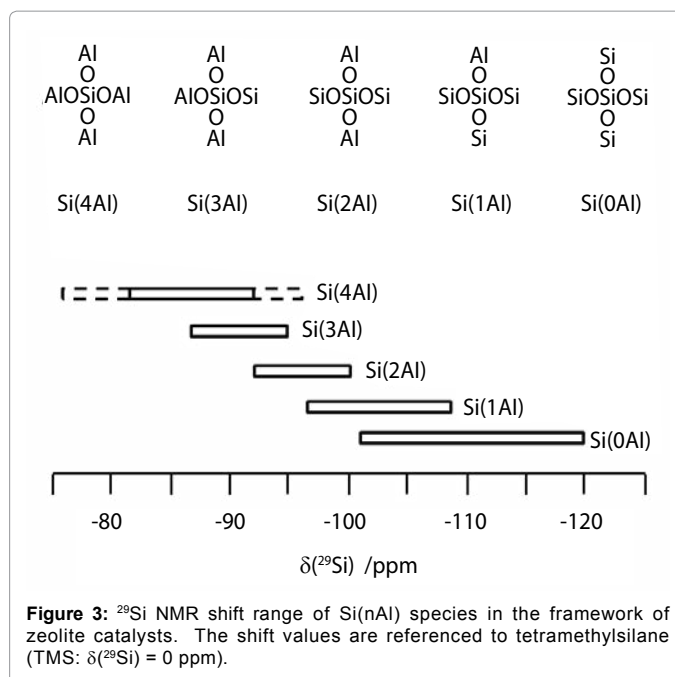


Figure 3: ^{29}Si NMR shift range of Si(nAl) species in the framework of zeolite catalysts. The shift values are referenced to tetramethylsilane (TMS: $\delta(^{29}\text{Si}) = 0$ ppm).

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