



Biaxial Q-shearing of ^{27}Al 3QMAS NMR spectra: Insight into the structural disorder of framework aluminosilicates



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ABSTRACT

In this contribution, we present the application potentiality of *biaxial Q-shearing* of ^{27}Al 3QMAS NMR spectra in the analysis of structural defects of aluminium units in aluminosilicates. This study demonstrates that the combination of various shearing transformations of the recorded ^{27}Al 3QMAS NMR spectra enables an understanding of the broadening processes of the correlation signals of disordered framework aluminosilicates, for which a wide distribution of ^{27}Al MAS NMR chemical shifts and quadrupolar parameters (i.e., second-order quadrupolar splitting and quadrupole-induced chemical shifts) can be expected. By combining the suitably selected shearing transformation procedures, the mechanisms of the formation of local defects in aluminosilicate frameworks, including Al/Si substitution effects in the next-nearest neighbouring T-sites, variations in bond angles, and/or variations in the physicochemical nature of charge-balancing counter-ions, can be identified. The proposed procedure has been extensively tested on a range of model aluminosilicate materials (kyanite, γ -alumina, metakaolin, analcime, chabazite, natrolite, phillipsite, mordenite, zeolite A, and zeolite Y).

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1. Introduction

Zeolites are microporous crystalline aluminosilicate molecular sieves with three-dimensional frameworks formed by SiO_4 and AlO_4^- tetrahedra sharing corners. The enormous variability of the arrangement of $\text{Si}(\text{Al})\text{O}_4$ tetrahedra results in more than 200 framework topologies with different architectures and dimensions of the zeolite pore/cavity system with the channel diameter ranging from 3.5 to 15 Å. The isomorphous substitution of Al atoms in the silicate framework results in the potential ability of the framework negative charge to stabilise well-defined counter-ion species, i.e., strongly acidic protons, bare metal ions, and metal-oxo and metallic species inside the defined pore system. Due to their local negative framework charge, these counter-ion species exhibit unique acidic or redox properties, which enable them to act as highly active sites for acid- and redox-catalysed reactions or as specific adsorption centres. The perturbation of framework tetrahedral Al atoms can occur and result in the formation of framework (FAI) and extra-framework (EFAl) Al-Lewis sites, which also represent significant catalytic and sorption centres. The combination of the variability of well-defined active sites and the variability of the well-defined channel/cavity system

with a large inner surface area has led to the use of zeolites as catalysts or sorbents in numerous chemical processes [1–5].

The formation and performance of both adsorption and catalytic centres in zeolites are either governed by framework Al atoms or framework and extra-framework Al species that act as such centres. Thus, the arrangement of framework Al atoms in the zeolite framework (in individual crystallographic sites of tetrahedral-forming zeolite frameworks and in various Al–O–(Si–O)_x–Al sequences) and the nature of perturbed Al sites represent crucial parameters of zeolite catalysts and sorbents [6]. The Al atoms in the regular framework structure can be characterised by a limited set of well-defined bond angles and lengths reflecting the arrangement of Al atoms in individual crystallographic T sites. In this respect, the local arrangement of Al atoms in the framework of Si-rich ($\text{Si}/\text{Al} > 8$) zeolites, such as ferrierite and ZSM-5, has been successfully described [7,8]. In contrast to framework Al atoms, perturbed Al atoms forming Al-Lewis acids can be described by continuous distributions of atomic environments of such Al species resulting in the limited knowledge of the nature of these species although they often play important role. Quantitative and qualitative characterizations of structural defects, extra-framework aluminium species, and other minor components are thus necessary to understand the function, property control, and further development of zeolites [6].

The application of X-ray powder diffraction analysis of Al atoms is strictly limited due to the similar electron density of the Al^{3+} and Si^{4+} ions of the zeolite framework. In addition, the recently

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reported application of X-ray diffraction experiments is suitable only for large monocrystals with uniform Al distributions [9]. In recent decades, developments in high-resolution solid-state NMR spectroscopy have resulted in the establishment of ss-NMR spectroscopy as a powerful tool for the precise characterisation of zeolite structures. Solid-state NMR spectroscopy has become an efficient tool for the study of aluminium in zeolites because of the high sensitivity of nuclear spin interactions to the oxygen coordination, local symmetry, and concentration of framework and extra-framework species. The primary information that can be obtained from ^{27}Al MAS NMR spectra is related to the coordination geometry of Al–O environments. However, one-dimensional spectra are affected by the quadrupolar interactions of ^{27}Al spins with electric field gradients (EFG) that cause an asymmetric broadening of spectral lines. This broadening in well-defined crystalline systems is attributed to second-order quadrupolar splitting [10,11]. For disordered and amorphous systems, the second-order quadrupolar splitting is combined with the distribution of the isotropic chemical shift and the distribution of electric field gradients. To separate or eliminate these contributions, advanced NMR acquisition and processing techniques are required.

An elegant method of overcoming the problem of the signal broadening of quadrupolar nuclei and increasing spectral resolution is the application of multiple-quantum magic angle spinning (MQMAS) NMR spectroscopy [12]. This technique combines magic angle spinning with radio-frequency spin manipulation to refocus quadrupolar broadening. Subsequent developments have led to many modifications of the original MQMAS NMR technique, providing substantially enhanced sensitivity (e.g., z -filter, split- t_1 , FAM, DSF, and satellite-transition experiments [13–18]). In general, the resulting 2D MQMAS NMR spectra provide three independent spectral contributions: isotropic chemical shift, isotropic quadrupole induced shift, and quadrupolar anisotropy, which are each aligned in different directions. As these directions are not perpendicular or parallel to the frequency axes (F_1 , F_2), the recorded raw data matrix is usually processed using a specific shearing transformation to obtain a 2D MQMAS NMR spectrum that allows for a straightforward interpretation. The most frequently used shearing transformation is *isotropic-shearing* (ISO-shearing). The ISO-shearing transformation aligns the anisotropic broadening along the direct dimension (F_2), leaving the indirect dimension (F_1) free of any anisotropic contribution [19]. Consequently, the skyline projection in the F_1 dimension is highly resolved, revealing the NMR signals of individual structure units. ISO-shearing is particularly suited for crystalline materials.

Numerous structural studies of framework aluminosilicates using ^{17}O , ^{23}Na , and ^{27}Al MQMAS NMR spectroscopy have been presented [20–22]. However, in spite of the important advantages of this experimental approach, the problems arising due to the incomplete separation of individual spin contributions have remained unresolved. In particular, disordered materials exhibit a large distribution of isotropic chemical and quadrupole-induced shifts, complicating the understanding of the ISO-sheared MQMAS NMR spectra. Thus, alternative approaches of shearing transformation have been tested [23,24]. For instance, *Q-shearing* was applied to systems in which the inhomogeneous line width was greater than the anisotropic second-order quadrupolar broadening. Applying this procedure, the indirect dimension F_1 became a function of quadrupolar parameters, whereas the distribution of isotropic chemical shifts was aligned along the F_2 axis. Recently, both ISO- and Q-shearing transformations have been extended by the secondary shearing factor, which also manipulates NMR frequencies in the direct spectral dimension [25]. This *biaxial shearing* allows for complex manipulation of the multiple-quantum spectrum and can result in specific separation of individual spectral contributions. It has been suggested that this

Table 1

The Si/Al_{FR} ratios calculated from ^{29}Si MAS NMR spectra and Si/Al ratios determined by XRF.

	ANA	CHA	NAT	PHI	MOR	LTA	ZeoY
Si/Al _{FR}	2.2	2.6	1.5	2.2	11	1	2.4
Si/Al (XRF)	2.0	2.4	1.5	2.1	10.4	1	2.4

processing may contribute to the understanding of the complicated MQMAS NMR spectra of disordered solids. The recently published studies have indicated certain advantages in the analysis of ^{17}O and ^{27}Al MQMAS NMR spectra of geopolymers [25,26], but a systematic study is still needed.

To fill this gap, we performed a series of ^{27}Al MQMAS NMR experiments, including various spectral shearing transformations of a range of disordered aluminosilicate solids. As a model system, we first used kyanite, a system with distinct and well-resolved aluminium sites with remarkably different quadrupolar parameters. In contrast, synthetic γ -alumina and metakaolin were used as model amorphous solids because they have Al sites significantly differing in their chemical shifts. Natural and synthetic zeolites with a variable degree of framework disorder were then analysed based on the results obtained for the model aluminosilicates. The purposes of the present study were to determine a suitable procedure to identify the principal contributions inducing a broadening of ^{27}Al 3QMAS NMR signals, to determine how to separate and quantify these contributions, and to determine how to assign individual resonances to their corresponding structure units (aluminium T sites). Our effort was primarily focused on developing an optimal shearing procedure for the accurate discrimination of framework and extra-framework aluminium species in zeolites. To support the results experimentally, we applied a simple ^{27}Al - $\{^1\text{H}\}$ CP/MAS NMR experiment allowing selective excitation of aluminium sites interacting with proton species (H_2O , OH^- , H^+ , etc.). Additional improvements based on ^{27}Al - $\{^1\text{H}\}$ REDOR 3QMAS [27] and ^{27}Al - $\{^1\text{H}\}$ CP-3QMAS [28] experiments are discussed.

2. Experimental

2.1. Materials

Kyanite (KYA; Moravice, Czech Republic), γ -alumina (ALU; SASOL), and metakaolin (MKA; Sedlec, Czech Republic) served as model materials to optimise the individual experimental methods. Typical representatives of natural zeolites differing in their framework structure and chemical composition involved in this study included natural analcime (ANA; Mojzír, Czech Republic); chabazite (CHA Sebužin, Czech Republic); natrolite (NAT; Soutesky, Czech Republic); phillipsite (PHI; Cirkvice, Czech Republic); and the synthetic zeolites mordenite (MOR; TOSOH, $\text{Na}^+/\text{Ca}^{2+}$ form), zeolite A (LTA; VURUP, Na^+ form), and zeolite Y (ZeoY; TOSOH, Na^+ form). The chemical compositions obtained by XRF analysis (Si/Al) and ^{29}Si NMR spectroscopy (Si/Al_{FR}) are summarised in Table 1 (see Supporting Information for complete elemental composition).

2.2. X-ray powder diffraction analysis

The XRPD patterns were collected with a Siemens D5005 powder X-ray diffractometer equipped with a graphite monochromator and scintillation counter using $\text{CuK}\alpha$ radiation in Bragg–Bretano geometry. Each sample was measured between 3° and 40°

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