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Review (Special Issue for Excellent Research Work in Recognition of Scientists Who Are in Catalysis Field in China)

^{17}O solid-state NMR studies of oxygen-containing catalysts

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ABSTRACT

Oxygen-containing catalysts have a broad range of applications, and it is important to understand the structure–property relationships of these materials. In the past 30 years, ^{17}O NMR spectroscopy, which is sensitive to the local structure of oxygen, has been used to study various catalysts, including non-framework oxides, zeolites, heteropoly acids, layered double hydroxides (LDHs) and metal-organic frameworks (MOFs). The results from these studies have provided rich information on the structure and interactions of oxygen catalysts. This review summarizes significant progress in ^{17}O solid-state NMR studies of oxides and related catalysts.

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1. Introduction

The only NMR-active stable isotope of oxygen, ^{17}O, has a large chemical shift range, greater than 1000 ppm, making it a very sensitive structure probe. Quadrupolar interactions of ^{17}O (I = 5/2), i.e., the interaction between the quadrupole moment and the electric field gradient (EFG) at the oxygen site, can also be used to investigate local structures. The size of the quadrupolar interaction is usually represented by the quadrupolar coupling constant (C_Q), and the asymmetry parameter (η) is a measure of the deviation of the EFG from axial symmetry ($0 \le \eta \le 1$). In addition, oxygen has a large ionic radius and is usually present at key points in the structure, therefore it is intimately involved in adsorption and catalytic steps. ^{17}O solid-state NMR spectroscopy should therefore be an ideal method for obtaining detailed information on the structures of catalysts, and the adsorption and catalytic processes.

^{17}O solid-state NMR studies of catalysts are not routine, mostly because of the low natural abundance of ^{17}O (0.037%) and the high cost and difficulties associated with isotopic labeling, the relatively low gyromagnetic ratio, and the significant spectral broadening caused by quadrupolar interactions, which make high-quality data hard to acquire and NMR spectra difficult to interpret. With the development of high external magnetic field strength and fast magic-angle spinning (MAS) techniques [1], high-resolution ^{17}O NMR spectroscopy is now used for a variety of solids, including simple oxides and zeolites [2–6]. Relatively new methods that can further improve spectral resolution include double rotation (DOR) [7], dynamic angle spinning (DAS) [7], multiple quantum MAS (MQMAS) [8], and satellite transition MAS [9]. Among these techniques, two-dimensional (2D) MQMAS is most frequently used. The

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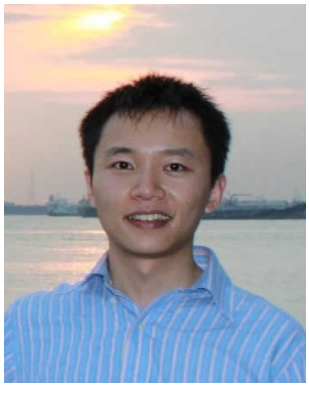
basic concept in this method is that the anisotropic second-order quadrupolar line broadening term under multiple-quantum evolution can be chosen to have the opposite sign to that under single-quantum evolution, therefore a pure isotropic echo can be formed, generating a high-resolution isotropic dimension.

Once high resolution has been achieved, the dipolar interaction between oxygen and another nuclear spin, which is directly related to the internuclear distance and interactions in the catalyst, can be investigated using double-resonance techniques such as cross-polarization (CP) [10], rotational echo double resonance (REDOR) [11], and transfer of populations in double resonance (TRAPDOR). In these experiments, the intensity of the ^{17}O signal arising from a specific species depends on the dipolar interaction involving ^{17}O, which is inversely proportional to the cube of the internuclear distance. The distance between oxygen and another nucleus or the through-space proximity can therefore be determined. More detailed information on the background principles of solid-state NMR spectroscopy can be found in other review papers [12,13].

2. Oxide catalysts (non-framework)

2.1. Simple oxides

Many simple oxides are extensively used as catalysts and/or catalyst supports, and they are very important in industrial catalysis. For example, basic MgO materials have been used for dehydrohalogenation transformations [14] and CO_2 reforming of CH_4 [15], and acidic γ-Al_2O_3, which has a large surface area, is one of the most widely used catalyst supports [16,17]. ^{17}O labeling of oxides can be achieved using ^{17}O-enriched water as the starting material [2,3,5,6], or by simply heating oxides in $^{17}O_2$ at high temperatures [4]. MgO is isostructural with NaCl, therefore the O and Mg ions in MgO have cubic symmetry, resulting in small EFGs (ideally zero) at O and Mg sites. ^{17}O NMR spectra are therefore dominated by chemical shift distributions instead of quadrupolar effects. Fiske et al. [18] observed that the ^{17}O chemical shift of MgO changes from 47 to 57 ppm with increasing temperature from room temperature to 1300 °C. The chemical shift change to higher frequency is induced by the increased orbital overlap, which originates from the increased thermal vibrations of ions at higher temperatures. Careful study showed that two peaks, at 47 and 42 ppm, are present in the ^{17}O NMR spectrum of MgO, from bulk and surface species, respectively [19,20]. Walter et al. [21] first studied the structures of α-Al_2O_3, AlO(OH), $Al(OH)_3$, and different types of transitional alumina materials, including the most important alumina catalyst, γ-Al_2O_3, using ^{17}O MAS NMR. Only one signal, corresponding to OAl_4 with C_2 symmetry, is observed in the ^{17}O MAS NMR spectrum of α-Al_2O_3, consistent with the structure obtained from single-crystal studies. The lattice structure of γ-Al_2O_3 is different from that of α-Al_2O_3, but similar to that of spinel $MgAl_2O_4$, and the ^{17}O MAS NMR spectrum of γ-Al_2O_3 has two overlapping signals near 70 ppm. The narrower and broader components can be assigned to OAl_4 and OAl_3, respectively; the latter has a larger quadrupolar coupling constant (C_Q) because of the disordered structure. The resonances for hydroxyl oxygen from AlO(OH) and $Al(OH)_3$ can be observed using $^1H\rightarrow^{17}O$ CP NMR spectroscopy [21], and the same method can be used to identify the hydroxyl sites in γ-Al_2O_3, although this signal cannot be observed using single-pulse ^{17}O MAS NMR spectroscopy. This can be ascribed to the much smaller amount of surface hydroxyl species compared with bulk species in the sample, which was obtained by calcination of ^{17}O-labeled boehmite at 500 °C. Isotopic labeling of Al_2O_3 is also affected by the supported catalytic active species. Wang et al. [22] observed that the ^{17}O NMR signal for Ag/α-Al_2O_3 was much more intense than that for bare α-Al_2O_3, both of which were enriched with $^{17}O_2$ at 300 °C, as a result of activation of $^{17}O_2$ molecules by the Ag catalyst on the γ-Al_2O_3 support. The C_Qs of the oxygen ions in SiO_2, which is also an important catalytic component [23–25], are much larger than those of MgO, because Si–O–Si is less ionic than Mg–O–Mg [3]. Advanced high-resolution techniques are therefore often needed to achieve high spectral resolution. For example, Grandinetti et al. [26] used ^{17}O DAS NMR spectroscopy to study the structure of a silica polymorph, i.e., monoclinic coesite. The 2D data show that there are five distinct oxygen sites in coesite and the ^{17}O quadrupolar parameters (C_Q and the asymmetry parameter η) change as a function of the Si–O–Si bridging bond angle. A combination of one-dimensional static, MAS, and MQMAS NMR techniques was used by van Eck et al. [27] to detect the hydroxyl groups in a silica gel produced using a sol-gel method. Signals arising from Si–O–Si linkages and hydroxyl oxygen are observed. The T_1 relaxation time is much shorter for hydroxyl oxygen because of



Luming Peng *(Nanjing University)* ***received the Catalysis Rising Star Award in 2012****, which was presented by The Catalysis Society of China. Professor Luming Peng received his B.S. degree in Chemistry from Nanjing University in 2001 and his Ph.D. degree in Chemistry from State University of New York at Stony Brook (supervised by Prof. Clare P. Grey, FRS) in 2006. He did postdoctoral research on the structure of oxide glasses in Prof. Jonathan Stebbins's lab at Stanford University from 2006 to 2008. He jointed School of Chemistry and Chemical Engineering at Nanjing University as an associated professor in 2008 and was promoted to full professor in 2014. His research interests include solid-state NMR spectroscopic study of catalysts, as well as environmental and energy related materials. He has published more than 60 peer-reviewed papers.*

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