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

Li Shen, Luming Peng *

Key Laboratory of Mesoscopic Chemistry of MOE and Collaborative Innovation Center of Chemistry for Life Sciences, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, Jiangsu, China

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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 ($0 \leq \eta \leq 1$). 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

* Corresponding author. Tel: +86-25-83686793; Fax: +86-25-83686251; E-mail: luming@nju.edu.cn

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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 $\gamma\text{-Al}_2\text{O}_3$, 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 $^{17}\text{O}_2$ 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 $\alpha\text{-Al}_2\text{O}_3$, $\text{AlO}(\text{OH})$, $\text{Al}(\text{OH})_3$, and different types of transitional alumina materials, including the most important alumina catalyst, $\gamma\text{-Al}_2\text{O}_3$, 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 $\alpha\text{-Al}_2\text{O}_3$, consistent with the structure obtained from single-crystal studies. The lattice structure of $\gamma\text{-Al}_2\text{O}_3$ is different from that of $\alpha\text{-Al}_2\text{O}_3$, but similar to that of spinel MgAl_2O_4 , and the ^{17}O MAS NMR spectrum of $\gamma\text{-Al}_2\text{O}_3$ 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 $\text{AlO}(\text{OH})$ and $\text{Al}(\text{OH})_3$ can be observed using $^1\text{H} \rightarrow ^{17}\text{O}$ CP NMR spectroscopy [21], and the same method can be used to identify the hydroxyl sites in $\gamma\text{-Al}_2\text{O}_3$, 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 $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ was much more intense than that for bare $\alpha\text{-Al}_2\text{O}_3$, both of which were enriched with $^{17}\text{O}_2$ at 300 °C, as a result of activation of $^{17}\text{O}_2$ molecules by the Ag catalyst on the $\gamma\text{-Al}_2\text{O}_3$ support. The C_Q s 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 joined 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.

the high mobility of hydrogen. The majority of hydroxyl oxygens have a small C_Q (< 200 kHz), but a small number of hydroxyl sites have a larger C_Q (~ 3 MHz); both values are smaller than those of Si–O–Si (5–6 MHz).

Diamagnetic transition-metal oxides such as TiO_2 , V_2O_5 , and ZrO_2 are often the major components in catalytic materials. These oxides often have different crystal phases, and their catalytic properties are very different; for example, anatase is known to be more efficient than rutile in photocatalysis [28]. The sensitivity of the ^{17}O chemical shift to the oxide structure can therefore be used to identify different crystal phases of single metal oxides, and this is an important technique. ^{17}O NMR data show that there are only three-coordinated oxygen ions (OTi_3) in the three most important TiO_2 phases: anatase, rutile, and brookite. The ^{17}O chemical shifts in anatase and rutile occur at 557 and 591 ppm, respectively; two oxygen signals, at 552 and 584 ppm, are observed for brookite [29–31]. Similarly, different polymorphic forms of ZrO_2 (cubic, tetragonal, and monoclinic) can be distinguished based on the ^{17}O chemical shifts [32]. Two peaks, at 324 and 401 ppm, are observed for monoclinic ZrO_2 , from the OZr_4 and OZr_3 environments, respectively, whereas a single resonance, from OZr_4 , is seen in the ^{17}O NMR spectrum of cubic (355 ppm) or tetragonal (378 ppm) ZrO_2 . Surface hydroxyl species are also important in these catalysts. The ^{17}O signal from Ti–OH in titanium oxopolymers can be observed in static CP NMR spectra; the absence of this signal in single-pulse NMR spectra is attributed to the low concentrations of these species [33]. In metal oxides with metals in higher oxidation states ($> +4$), the concentration of terminal oxygen species ($\text{M}=\text{O}$) can be significant. For example, three different types of oxygen site, corresponding to vanadyl ($\text{V}=\text{O}$), doubly coordinated ($\text{V}-\text{O}-\text{V}$ or V_2O), and triply coordinated (V_3O) species, can be observed in the ^{17}O NMR spectrum of crystalline V_2O_5 , which is an important catalyst for oxidation reactions. Although water molecules preferentially adsorb at vanadyl oxygen ($\text{V}=\text{O}$) sites on a dehydrated V_2O_5 gel at room temperature, the ^{17}O NMR results show that ^{17}O atoms are readily exchanged into all the sites in the gel structure, implying that these V-containing layered materials are good candidates for low-temperature oxidation catalysts.

2.2. Nanosized oxides

Nanostructured oxides have large surface areas and often have better catalytic properties than their bulk counterparts. The characterization of the surface and subsurface structures of nanomaterials, which are expected to control the catalytic properties, attracts much attention. Although microscopy plays an important role, because such techniques provide little chemical bonding information and the volumes sampled may not be representative of the whole sample, complementary methods are required. NMR spectroscopy is an ideal method for studying nanostructures because it is sensitive to the short-range order of all the resonant nuclei in the sample investigated. However, NMR spectroscopy has only occasionally been used to study nanomaterials. Limited research has been performed, including investigation of MgO and TiO_2 nanoparti-

cles. Chadwick et al. [19] found that the ^{17}O NMR spectra vary depending on the size of the MgO nanophase, and three different MgO -like environments are observed, i.e., two related to bulk-like sites, and one related to surface layer sites. Scolan et al. [34] investigated titanium oxo-organo clusters and anatase nanoparticles using ^{17}O MAS NMR spectroscopy. A number of oxygen ions can be identified, including surface oxo species (2- and 3-coordinated oxygen ions and $\text{acac}-\text{O}-\text{Ti}$), Ti–OH, surface water ($\text{H}_2\text{O}-\text{Ti}$), and three-coordinated oxygen ions in the bulk, based on the ^{17}O chemical shifts.

More recently, Wang et al. [35] developed a new NMR technique for examining the oxygen ions on the first, second, and third surface layers (Fig. 1), hydroxyl groups on the first layer, and oxygen ions near an oxygen vacancy, of nanomaterials. The technique was developed using ceria nanostructures, and it was found that these oxygen species have distinct chemical shifts (δ_{iso}) and can be distinguished from bulk oxygen ions. In particular, the resonant frequency of lower-coordinated surface oxygen ions (OCe_3) in ceria is much higher (~ 1040 ppm) than that of bulk sites (OCe_3 , 877 ppm). NMR spectroscopy also shows that fast exchanges occur between the surface oxygen ions and water, therefore ^{17}O -enriched water can be used to selectively label the surface with ^{17}O . For ceria nanorods (diameter ~ 8 nm) with exposed (111) facets, only the top two layers of oxygen ions are enriched by contact with ^{17}O -enriched water, demonstrating the high sensitivity and selectivity of the method. The surface hydroxyl groups ($\text{Ce}-\text{OH}$) can also be observed using this approach and these sites have a much larger C_Q and much lower chemical shift than non-protonated first- and second-layer oxygen ions. This approach enables these surface sites, which are the most relevant to catalysis, to be tracked during a catalytic process. Density functional theory (DFT) calculations on ^{17}O chemical shifts play a critical role in making spectral assignments (Fig. 1(b)); the results show that

Fig. 1. (A) ^{17}O NMR spectra of enriched ceria nanoparticles at different temperatures and external fields compared with the ^{17}O NMR spectrum of micron-sized ceria (bulk ceria), and summary of chemical shifts predicted using structural model shown in (B). The spectra obtained at 14.1 and 9.4 T were acquired at spinning speeds of 55 and 20 kHz, respectively. (B) Structural model of ceria used in DFT calculations. Red and white spheres represent oxygen and cerium ions, respectively. The exposed surface is (111) and the calculated chemical shift of ^{17}O in each layer is shown on the right-hand side. Reprinted with permission from [35].

in addition to depending on the number of layers from the surface, the chemical shift also strongly depends on the nature of the surface, i.e., distinct chemical shifts are expected for nanostructured oxides exposing different crystal facets. The NMR chemical shift can therefore be used to determine the exposed surfaces and the morphologies of nanocrystals, and to explore related catalytic processes.

2.3. Complex oxide catalysts

Complexes consisting of two or more oxides are often used as catalysts and catalyst supports. ^{17}O NMR spectroscopy is a powerful tool for investigating the structures at oxide interfaces. Holland et al. [36] used ^{17}O MAS NMR spectroscopy to investigate the structure of a $(\text{TiO}_2)_{0.18}(\text{SiO}_2)_{0.82}$ xerogel catalyst for the epoxidation of cyclohexene. The results show that the dominant signal appears at around 0 ppm, from Si–OH and Si–O–Si environments, and a signal is observed at 220 ppm, corresponding to Si–O–Ti linkages. The absence of a signal at 360 or 530 ppm, from OTi_4 or OTi_3 , respectively, proves that there is no phase separation and confirms that Ti is homogeneously mixed into the silica network in the catalyst. Catalytic test results indicate that the catalytic activity depends on the amount of accessible Si–O–Ti surface species, demonstrating that ^{17}O NMR spectroscopy can provide key information on the structures and properties of TiO_2 – SiO_2 -based materials. ^{17}O NMR spectroscopy also plays an important role in characterization of the structures of $(\text{ZrO}_2)_x(\text{SiO}_2)_{1-x}$, TiO_2 – ZrO_2 – SiO_2 , $(\text{Ta}_2\text{O}_5)_x(\text{SiO}_2)_{1-x}$, and Nb_2O_5 – SiO_2 catalysts [37–41].

Many catalytic active oxides are supported on high surface area oxides such as Al_2O_3 and SiO_2 , and the catalytic properties can be modified by the interactions between different oxides. To increase the catalytic activity and selectivity, the structure and interactions of the catalytic active species and the support should be well controlled. Merle et al. [42] successfully used ^{17}O NMR spectroscopy to study the catalyst structures and interactions between inorganic carriers and supported catalysts. When transition-metal species are grafted onto the catalyst support, i.e., SiO_2 in this case, different ^{17}O NMR signals emerge, because it is the oxygen ions that connect with Si in the support or the metal ions. Selective labeling of the support surface was used to increase the sensitivity of this approach. The sample was first dehydrated at high temperature, up to 1000 °C, rehydrated with ^{17}O -enriched water, and calcined at 200 °C (denoted by SiO_2^{*200}). The ^{17}O MQMAS spectrum of the tungsten derivative shows two silanol groups centered at $\delta_2 = 3$ and 9 ppm, corresponding to SiOH-1 and SiOH-2, respectively. These signals lie along the diagonal, indicating a chemical shift distribution; the same affiliation is found in the tantalum derivative, with weaker signals (Fig. 2(a) and (c)). For both materials, the major signal, ascribed to SiOSi-1, shows line broadening, as a result of second-order quadrupolar effects, and the other signal, from SiOSi-2, is dominated by the chemical shift distribution. There are significant differences in the high-frequency region. The signal with a large chemical shift distribution centered at 220 ppm is assigned to SiOTa (Fig. 2(b)) for Ta– SiO_2^{*200} , whereas the spectrum of W– SiO_2^{*200} has two components:

Fig. 2. ^{17}O MQMAS NMR spectra at 18.8 T of (a, b) Ta– SiO_2^{*200} and (c and d) W– SiO_2^{*200} . Conditions: (Ta– SiO_2^{*200}) ns = 6400, rd = 1 s, t_1 = 36, acquisition time = 64 h, MAS rate = 20 kHz; (W– SiO_2^{*200}) ns = 7200, rd = 1 s, t_1 = 42, acquisition time = 84 h, MAS rate = 20 kHz. Reprinted with permission from [42]. Copyright 2012 American Chemical Society.

the first signal, centered at about 152 ppm, which is dominated by quadrupolar effects, is assigned to SiOW-1, and the second signal, at 200–120 ppm, is ascribed to SiOW-2. These results show that ^{17}O NMR spectroscopy can be used to identify different oxygen species in supported catalysts.

Other examples include supported V_2O_5 catalysts ($\text{V}_2\text{O}_5/\text{TiO}_2$, $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$, and $\text{V}_2\text{O}_5/\text{SiO}_2$), which can be used for catalytic oxidation. ^{17}O NMR results show that dehydrated surface vanadia species are heterogeneous and oxygen species are in V=O or V–O–V/V–O–M (M is from the support) environments [43]. In addition to oxygen exchange with surface vanadia species, significant exchange occurs between the oxide support and gas-phase O_2 for these catalysts; this is important for understanding the mechanisms of related reactions.

3. Zeolites

Zeolites are a family of crystalline aluminosilicate frameworks with well-defined cavities and channels, formed by corner sharing AlO_4 and SiO_4 tetrahedra. They are extensively used in industrial catalysis, e.g., in catalytic cracking in petroleum refining. Much research has been performed on their porous structures and specific acidities/basicities, which are critical in controlling the selectivities and activities of zeolite-based catalysts. In addition to key information on the binding sites and interaction strengths of molecules adsorbed on the zeolitic framework, the ordering of Al- and Si-centered tetrahedra, which significantly affects framework formation and the reactivity of the material, is also very important. According to Lowenstein's rule, oxygen ions cannot connect two Al ions, i.e., Al–O–Al linkages are forbidden in zeolites and only Si–O–Si and Si–O–Al linkages exist. Oxygen is the major component of zeolites and is therefore more likely to be a binding site, so ^{17}O

NMR spectroscopy can provide valuable information on the structures and interactions of zeolites, which may not be accessible using ^1H , ^{27}Al , or ^{29}Si NMR spectroscopies.

3.1. Oxygen sites in framework

Because of the importance of zeolites, they were among the first materials to be investigated using ^{17}O NMR spectroscopy [5,6]. Isotopic labeling with ^{17}O can be achieved using ^{17}O -enriched water directly in sample preparation [5,6], or by heating the zeolites with ^{17}O -enriched water under hydrothermal conditions [44–51] or $^{17}\text{O}_2$ at high temperatures [44,52–61]. Si–O–Si and Si–O–Al sites are both observed; however, the two signals overlap significantly in static or MAS spectra, because of the large C_Q s and similar isotropic chemical shifts. Two resonances can be fitted and separated according to the different C_Q s (i.e., 5–6 MHz for Si–O–Si and 3–4 MHz for Si–O–Al); however, the resolution is insufficient to distinguish crystallographically different Si–O–Si and Si–O–Al sites [5,6]. With the development of high-resolution techniques for quadrupolar nuclei, such as DOR, DAS, and MQMAS, crystallographically distinct sites can be resolved using ^{17}O NMR spectroscopy [26,46,52]. For example, four Si–O–Si sites were distinguished in siliceous zeolite Y [52], and four and three Si–O–Al environments were resolved in zeolite Na, K-LSX, and Na-A [46], respectively. However, the high resolutions observed in these studies are achieved because only Si–O–Si linkages are present in the siliceous zeolite, whereas there are only Si–O–Al groups in zeolites with Si/Al = 1, assuming that Lowenstein's rule holds. In more general cases, for Al-containing zeolites (Si/Al > 1), these advanced methods enable the distinction of Si–O–Si from Si–O–Al, but the resolution is not high enough to separate crystallographically different sites [45].

The identification of crystallographically distinct oxygen sites using ^{17}O NMR is challenging, because spectral features can rarely be easily assigned, for example, based on the relative intensities of the resolved signals [48,49,61]. Ab initio calculations and experimental work on model systems have been performed to correlate ^{17}O NMR parameters (i.e., δ_{iso} , C_Q , and η) with the structural characteristics of zeolites (e.g., T–O–T' bond angles, T/T'=Si or Al). For example, Farnan et al. [62] showed that C_Q increased, whereas η slightly decreased, with increasing Si–O–Si angle in silicate glasses. Several calculation results support this conclusion [63–69], but the correlation between C_Q (or η) and the Si–O–Si angle is weak [53]. In zeolites with high Al contents, such as LSX and A zeolites, the linear relationship between δ_{iso} and the Si–O–Al angle holds [46,49]. Similar relationships were observed more recently, between δ_{iso} or C_Q of ^{17}O and the Al–O–P angle in aluminophosphate zeolites [70]. However, Bull et al. [53] performed calculations to help spectral assignments and observed no dependence of δ_{iso} on the Si–O–Si angle in ferrierite. It was concluded that the ^{17}O NMR chemical shifts, which are affected by the atoms in the second and third coordination shells of oxygen, are extremely sensitive structure probes. This is why no simple correlation can be found between chemical shifts and bond angles.

Although Lowenstein's rule holds for most zeolites, ^{17}O

Fig. 3. ^{17}O 3QMAS spectra of ^{17}O -enriched stilbite. In these 2D spectra, isotropic spectra appear in the F_1 dimension and are free of second-order quadrupolar broadening. In the F_2 dimension, spectra that are distorted versions of standard MAS spectra appear. Contour lines mark intensities at equal intervals from 3% to 100% of the maximum, with an extra contour at 4.2% inserted to show the shapes of the low-intensity features. "C" marks the Al–O–Al peak center predicted from recent data on crystalline NaAlO_2 , and "G" marks that for an aluminous sodium aluminosilicate. Reprinted with permission from [50].

MQMAS spectroscopy has shown the presence of Al–O–Al linkages in the natural zeolite stilbite (Fig. 3) [50]. Quantitative ^{17}O NMR results show that the concentration of Al–O–Al is small (~3%) and corresponds to a deviation of 15% from Al avoidance; however, this amount is important for modeling free energy and phase equilibria in zeolites.

Recently, ^{17}O NMR spectroscopy has been used to study the oxygen environments in aluminophosphate zeolites [70,71]. Only broad or overlapping resonances can be observed for Al–O–P environments using ^{17}O MAS NMR spectroscopy of highly crystalline samples, because of broadening of the quadrupolar interactions and/or chemical shift distributions. Higher-resolution spectra can be obtained using ^{17}O DOR or MQMAS NMR spectroscopy, enabling partial distinction of crystallographically different oxygen sites [70]. This study also showed that ^{17}O labeling of aluminophosphate zeolites could be achieved using a highly efficient ionothermal method [70], which only requires a small amount of water, and this approach can be extended to the preparation of various ^{17}O zeolite analogs [72].

3.2. Effects of extraframework species

3.2.1. Brønsted acid protons

Although ^{17}O NMR spectroscopy has been providing valuable information on Si–O–Si and Si–O–Al groups since the 1980s, the oxygen ions at Brønsted acid sites (Si–O(H)–Al), which are often responsible for the activities of zeolites, were not detected in ^{17}O NMR spectra until the 2000s. Peng et al. [57] studied

the zeolite HY (Si/Al = 2.6), which has a significant amount of Brønsted acid sites, and were able to detect the oxygens at Brønsted acid sites using high-field ^{17}O MAS NMR techniques. The signals at -24 ppm appear as a shoulder peak in the single-pulse spectra, which are dominated by resonances from Si–O–Si and Si–O–Al linkages; $^1\text{H} \rightarrow ^{17}\text{O}$ CP MAS NMR or $^{17}\text{O} \rightarrow ^1\text{H}$ REDOR NMR spectroscopy can select this signal (Fig. 4), proving that these oxygen species are in close proximity to protons and confirming that this resonance arises from oxygen ions at Brønsted acid sites. Line fitting of the experimental data and *ab initio* calculation results both show that Si–O(H)–Al sites are associated with large C_Q and η values, more than 6.0 MHz and 0.8, respectively; these values are significantly larger than those for Si–O–Si and Si–O–Al ($C_Q = 3.0\text{--}5.4$ MHz, $\eta = 0\text{--}0.4$). This also partly explains why these oxygen ions were not been observed for a long time.

CP and REDOR NMR methods can also be used to measure O–H distances, which are closely related to the acidities of Brønsted acid sites. Because of the large dipolar coupling between ^1H and ^{17}O , which are bound directly, a modified REDOR sequence has to be used. A comparison of the spectra obtained experimentally using $^1\text{H} \rightarrow ^{17}\text{O} \rightarrow ^1\text{H}$ CP-REDOR NMR spectroscopy and those from numerical simulations shows that the O–H distance in zeolite HY is in the range 0.098–0.101 nm [58], only slightly longer than the calculated O–H distances (0.097–0.098 nm), but much longer than the O–H distance extracted from neutron diffraction data for the majority of oxygen ions ($\text{O}_1\text{--H}_1 = 0.082$ nm, O_1 , 54% of all oxygen ions at Brønsted acid sites). This short distance obtained from neutron data is considered to be physically unreasonable; the fact that the distances determined using NMR spectroscopy are longer than the calculated distances can be ascribed to proton hopping or librational motion of OH groups [58]. The O–H distances measured using low-temperature NMR spectroscopy are shorter, indicating restricted motion and therefore larger effective dipolar coupling [54,56].

Fig. 4. ^{17}O – ^1H REDOR NMR spectra of zeolite HY. Spectra were acquired at 14.1 T with a spinning speed of 13 kHz. Dephasing time: 308 μs ; recycle delays: 1 s. The difference spectrum was obtained by subtracting the double-resonance spectrum from the control spectrum. Reprinted with permission from [57].

The signals from Si–O(H)–Al groups in the supercages and sodalite cages of zeolite HY can be resolved using ^1H NMR spectroscopy, therefore ^1H – ^{17}O heteronuclear correlation (HETCOR) NMR spectroscopy can be used to distinguish ^{17}O NMR signals arising from different Si–O(H)–Al sites (Fig. 5) [58]. ^{17}O signals corresponding to two different Brønsted acid sites in the supercages and sodalite cages of zeolite HY can be identified by extracting slices along the ^{17}O dimension at ^1H NMR shifts of 3.7 and 4.4 ppm, respectively. The NMR parameters can be simulated, and they are significantly different to those of framework sites (i.e., Si–O–Si and Si–O–Al).

Double-resonance NMR methods such as CP/HETCOR and REDOR can be conveniently used to study the oxygens at Brønsted acid sites, but they are of little use in observing framework sites (Si–O–Si and Si–O–Al). High-field ^{17}O MQMAS NMR spectroscopy enables the detection of framework Si–O–Si and Si–O–Al, and Si–O(H)–Al, in a single experiment [59]. The sensitivity to Si–O(H)–Al can be enhanced by using an ultrahigh field strength of 19.4 T to decrease the broadening caused by second-order quadrupolar effects, and high-power ^1H decoupling methods (e.g., two-pulse phase modulated) to minimize the linewidths [59].

3.2.2. Charge-balancing cations and water

Zeolite extraframework species such as charge-balancing cations and water molecules in the cavities and channels also have significant impacts on the ^{17}O NMR parameters of oxygen ions. For example, Freude et al. [46] studied the chemical shifts

Fig. 5. (a) 2D ^1H – ^{17}O HETCOR NMR spectrum of zeolite HY obtained at 17.6 T. Contact time = 80 ms; spinning speed = 13 kHz; recycle delay = 1 s. A total of 64 and 1024 points were acquired in the first and second dimensions, respectively, with 4800 scans per time increment, therefore the full 2D spectrum took 3 d + 14 h to acquire. Slices and simulations of the ^{17}O dimension corresponding to the Brønsted acid sites in the supercages (b and d) and sodalite cages (c and e) are shown. The dashed lines in the 2D spectrum show where the slices were taken. Reprinted with permission from [58]. Copyright 2007 American Chemical Society.

of oxygen in Si–O–Al in zeolite LSX as a function of the ionic radius of the charge-balancing cation. The results show that the larger the ionic radius, the higher δ_{iso} . Similar results were obtained by another group for zeolite A [48]. However, the radius of the cation is not the only factor involved. Although the radius of Rb^+ is similar to that of Tl^{3+} , δ_{iso} of the oxygen ions in Si–O–Al in zeolite Tl-A is 20 ppm higher than that in zeolite Rb-LSX, presumably because of the different electric charges on Rb^+ and Tl^{3+} [46].

Water molecules in zeolites also induce a positive shift of oxygen ions; for example, an additional high-frequency shift of about 4 ppm can be observed for hydrated zeolite M-LSX (M = alkali-metal ion, i.e., Li^+ , Na^+ , or K^+), because of the interactions between water molecules and the framework oxygen ions [46]. When alkali-metal ions are substituted by alkaline-earth metal ions, δ_{iso} can be dependent on the hydration level. For example, the NMR shift for O_1 environments in dehydrated Ca-A is 10 ppm higher than that in hydrated Ca-A; this can be ascribed to the loss of the hydrogen-bonded water molecules of the O_1 site in the dehydrated sample [60]. Water can also affect Brønsted acid sites; ^1H – ^{17}O HETCOR NMR spectroscopy shows a new resonance at $\delta(^1\text{H}) = 6.2$ ppm for zeolite H-MOR on water adsorption, arising from Brønsted acid sites hydrogen bonded to water [55]. Among the NMR parameters, C_Q undergoes the most significant change, and it decreases from ~ 6.3 MHz to 5.5 MHz after exposure of the zeolite sample to water.

3.3. Adsorbed molecules

Probe molecules in combination with NMR spectroscopy have been extensively used to investigate the acidities/basicities of zeolites [73,74]. Acetone can hydrogen bond to Brønsted acid sites [75], therefore acetone- d_6 was used to demonstrate the sensitivity of the ^{17}O resonance from oxygen ions at Brønsted acid sites to gas adsorption [57]. The ^1H – ^{17}O TRAPDOR fractions of zeolite HY after adsorption are much smaller than that of bare zeolite, indicating that the O–H distance increases because of the formation of hydrogen bonds and increased proton mobility (Fig. 6) [57]. The C_Q of Brønsted acid sites, determined by irradiating ^{17}O at an offset frequency, decreases from ~ 7 to 5 MHz, implying that the O–H bond distance increased from 0.097 to 0.102 nm, according to the calculation results based on the relationship between C_Q and the O–H distance [76].

For zeolites with alkali-metal ions as charge-compensating cations, the framework oxygen ions have relatively strong basicities. It is interesting to investigate how acid molecules can influence the framework oxygen ions. However, no reliable indication of base–acid interactions was found in a study performed recently on zeolite LSX [51].

4. Other O-containing catalysts

^{17}O solid-state NMR spectroscopy can be used to study other O-containing acidic and basic catalysts, the most important being heteropoly acids (HPAs), layered double-hydroxides (LDHs), and metal–organic frameworks (MOFs).

Fig. 6. Detection of Brønsted acid sites in zeolite HY using high-field ^{17}O -MAS-NMR techniques. (a) ^1H – ^{17}O TRAPDOR NMR spectra of zeolite HY obtained at 8.45 T, spinning speed 3 kHz, irradiation time 133 μs , recycle delays 10 s. Expansion of the isotropic resonance obtained in the control experiment is shown as an inset. A ^{17}O radio-frequency field strength (determined with H_2^{17}O) of 54 kHz was used. (b) Plot of ^1H – ^{17}O TRAPDOR NMR fraction as a function of ^{17}O carrier frequency offset at 8.45 T; spinning speed 6.67 kHz, irradiation time 133 μs , recycle delays 10 s; $\omega_1/2\pi$ (determined with H_2^{17}O) of 54 kHz was used. Reprinted with permission from [57].

4.1. Heteropoly acids

HPAs are a class of polybasic acids that are formed by the condensation of two or more types of inorganic oxyacid [77,78]. Of six distinct structures, Keggin-type HPAs are the most stable [79,80]; they have the general chemical formula $\text{H}_{8-x}\text{XM}_{12}\text{O}_{40}$, where X and M represent a central ion (such as Si^{4+} , P^{5+} , or Ge^{4+}) and a metal ion (such as W^{6+} or Mo^{6+}), respectively. Keggin-type HPAs have attracted a lot of interest because they have the best thermal stabilities, high acidities, and high oxidizing abilities, and can therefore be used as acidic and oxidative catalysts. Keggin-structured heteropolyanions (HPANs) have the formula $\text{XM}_{12}\text{O}_{40}^{x-8}$ and consist of a central tetrahedral structure (XO_4) surrounded by 12 metal–oxygen octahedral structures (MO_6) [81–83]. The 12 octahedra can be divided into four oxygen-corner-sharing groups, M_3O_{13} , which are formed by three edge-sharing octahedra, MO_6 . There are three types of outer oxygen ions in Keggin HPANs: terminal oxygen ($\text{M}=\text{O}$), and two types of bridging oxygen (corner-sharing $\text{M}=\text{O}-\text{M}$ and edge-sharing $\text{M}-\text{O}-\text{M}$).

Kozhevnikov et al. [82] first used ^{17}O MAS NMR spectroscopy to determinate the proton sites in solid dehydrated $\text{H}_3\text{PW}_{12}\text{O}_{40}$. The ^{17}O MAS NMR spectrum of solid dehydrated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ contains three signals, at 708 ± 5 ppm ($\text{W}=\text{O}$), 440 ± 3 ppm ($\text{W}-\text{O}-\text{W}$, corner sharing), and 400 ± 3 ppm ($\text{W}-\text{O}-\text{W}$, edge sharing). The resonance from the four internal $\text{P}-\text{O}-\text{W}$ oxygen ions is not observed because of lack of ^{17}O enrichment. The signal from the terminal $\text{W}=\text{O}$ oxygen ions is observed at a lower frequency (-60 ppm) in the solid than in solution, whereas the resonance of the bridging $\text{W}-\text{O}-\text{W}$ oxygen ions have the same shifts in both solid and solution spectra. The different chemical shifts of $\text{W}=\text{O}$ species in the solid and solution indicate that the terminal $\text{W}=\text{O}$ groups are the predominant protonation sites rather than the bridging $\text{W}-\text{O}-\text{W}$ oxygen species. However, in contrast to the results of this pioneering work, the studies performed by other groups suggest that the isolated acidic proton is located on a bridging oxygen ion [84–87]. Uchida et al. [84] showed that the ^{17}O NMR chemical shifts of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ are highly sensitive. In addition to the acidic proton positions, other factors such as the hydration level and crystallinity have significant impacts on the chemical shift. Definitive evidence that the second type (O_c) of bridging oxygen ($\text{Mo}-\text{O}-\text{Mo}$) and the terminal oxygen (O_t) ion ($\text{W}=\text{O}$) are the acidic sites in Mo HPA and W HPA Keggin structures, respectively, was provided by Ganapathy et al. [88]. The ^{17}O MAS NMR spectrum of solid $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ is similar to that of $\text{H}_3\text{PW}_{12}\text{O}_{40}$, except that the $\text{Si}-\text{O}-\text{W}$ signal appears at 18 ppm, because of fast $^{16}\text{O}/^{17}\text{O}$ exchange at these sites [83]. Once the protonation sites have been resolved, there are rich possibilities for investigating and correlating the structures and catalytic properties of HPAs.

4.2. Layered double-hydroxides

LDHs have the general formula $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2(\text{A}^{n-}_{x/n})_x \cdot y\text{H}_2\text{O}]$, in which divalent cations M^{2+} (e.g., Mg^{2+}) in a brucite-like environment are partly ($x\%$, $17 \leq x \leq 33$) substituted by trivalent cations M^{3+} (e.g., Al^{3+}). LDHs and their calcined products (layered double-oxides) have a wide range of applications, including adsorbents and catalysts [89–91].

Similar to zeolites, the key structural information includes the ordering of divalent and trivalent cations. Definitive evidence has only very recently been obtained using ^1H MAS NMR spectroscopy [92–95]. High-resolution ^1H NMR spectra can be obtained, in which different H species can be separated, but they have to be acquired at ultrafast spinning rates, making this approach instrumentally demanding. In addition, as the number of different anions in the interlayer region increases, the spectral resolution decreases significantly [96]. The results of most studies suggest that Mg_3OH and Mg_2AlOH groups are present in LDHs, but there are no MgAl_2OH or Al_3OH groups; however, this is still the subject of debate [95].

The introduction of ^{17}O can be performed efficiently by exploiting the “memory effect” [96], and ^{17}O NMR results show that ^{17}O provides a better structure probe. ^{17}O MQMAS NMR spectra of LDHs with OH^- in the interlayer spaces acquired at a medium MAS rate (20 kHz) clearly show two resolved signals,

Fig. 7. ^{17}O 3QMAS NMR spectra of LDHs at 9.4 T under MAS frequency of 23 kHz. Projections of the anisotropic and isotropic dimensions are shown on the top and left sides of the 2D spectra, respectively. Cross-sections (full lines) extracted parallel to the anisotropic dimension of the 2D 3QMAS spectrum for M-26.1-OH $^-$ at 53.0 (a) and 64.8 (b) ppm in F_1 , along with the best-fit simulation (dotted lines), are shown. The time needed to acquire each 2D spectrum ranged from 16 to 72 h. Reprinted with permission from [96].

from Mg_3OH and Mg_2AlOH species (Fig. 7), whereas ^1H NMR spectra of these samples, even at 60 kHz spinning, can barely resolve these groups. The slices extracted parallel to the anisotropic dimension can be simulated to extract NMR parameters, including δ_{iso} , C_Q , and η . The isotropic dimension signal can then be used to measure the relative intensities of the two sites, because they have similar quadrupolar product (P_Q) values. These results agree well with the non-random cation distribution model, in which Al–O–Al avoidance holds, as in the case of aluminosilicate zeolites.

Sahoo et al. [97] used ^{17}O NMR spectroscopy to show that there is rapid exchange between CO_2 and carbonated anions intercalated within LDHs, making these materials attractive for CO_2 storage or separation. Fast exchange between water and hydroxyl groups in the hydroxide layer was also observed by Zhao et al. [96]. ^{17}O NMR spectroscopy therefore also provides an approach to the study of the dynamics and interactions of external species and LDHs.

4.3. Metal–organic frameworks

MOFs are an emerging family of organic–inorganic porous materials with many potential applications, including catalysis, and gas separation and storage [98]. MOF structures are often determined using single-crystal X-ray diffraction, but this is non-trivial if suitable single crystals are unavailable. ^1H and ^{13}C solid-state NMR spectroscopies have been routinely used as complementary structural characterization techniques to in-

investigate the organic linkers in MOFs. Although oxygen is an important component of many MOFs (e.g., MOFs with carboxylate ligands or hydroxyl species, oxygen anions, or water associated with the metal center) [99–101], few examples of ^{17}O NMR spectroscopic characterizations of MOFs have been reported [102–104]. However, promising results show that ^{17}O NMR spectroscopy may be able to provide key information on MOF catalysts. For example, He et al. [103] showed that different oxygen environments in the MOF Zr–UiO-66, including oxygen atoms in carboxylate groups, $\mu_3\text{-O}^{2-}$ anions, and $\mu_3\text{-OH}$ species, could be conveniently distinguished using ^{17}O NMR spectroscopy. The adsorption of guest molecules significantly changes the ^{17}O NMR spectrum of MIL-53(Al), and phase transformations can therefore be monitored. Wang et al. [104] further demonstrated that ^{17}O NMR spectroscopy could be used to probe the metal– CO_2 binding strength in the MOFs CPO-27-Mg and -Zn.

5. Conclusions and perspectives

^{17}O solid-state NMR spectroscopy has been used to study a range of oxygen-containing catalysts. Although rich information has been obtained, most research has focused on the catalyst structures, and little information has been given on the interactions between the catalysts and adsorbed molecules, which are more important in catalysis. The limited number of studies is associated with the low sensitivities of surface sites, and the high costs of ^{17}O enrichment. However, the few reported results show that ^{17}O NMR parameters can be very sensitive to gas adsorption and binding to external species [35,57,58]. With the development of new surface-selective labeling [35] and new dynamic nuclear polarization methods [20], both of which can select surface species, the sensitivity will be much improved, and the cost of ^{17}O labeling can be significantly reduced. DFT calculations of ^{17}O NMR parameters, which give powerful assistance in spectral assignments [35,53,57,105], combined with solid-state ^{17}O NMR spectroscopy, will provide more information on the interactions between catalysts and adsorbed

molecules. This approach is expected to provide new strategies for the characterization of oxides and their catalytic applications.

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Graphical Abstract

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

Li Shen, Luming Peng*
Nanjing University

This review focuses on the use of ^{17}O solid-state NMR spectroscopy to study the structures of oxygen-containing catalysts and the interactions between the catalysts and adsorbed molecules.

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含氧催化剂的 ^{17}O 固体核磁共振谱学研究

沈 丽, 彭路明*

南京大学化学化工学院, 介观化学教育部重点实验室、生命化学协同创新中心, 江苏南京210093

摘要: 含氧催化剂在工业催化等多个领域有重要应用。氧离子半径很大, 而且往往出现在材料的关键位点, 所以一般认为氧与吸附和催化过程密切相关。 ^{17}O 是氧的唯一有核磁共振响应的稳定同位素, 其化学范围极宽(>1000 ppm), 能灵敏反映结构信息; 由于是四极核($I > 1/2$), 其四极耦合作用也能用于结构研究。因此, ^{17}O 固体核磁共振谱学应是一种能提供丰富催化剂结构信息的理想表征手段。然而, 目前 ^{17}O 固体核磁共振研究催化剂并非常规手段, 这主要是因为 ^{17}O 的天然丰度很低, 同位素标记较为昂贵和困难, 其较低的旋磁比和较大的四极耦合作用导致谱线加宽, 难以获得高质量的谱图并加以解析。随着高磁场和高速魔角旋转等技术的发展, ^{17}O 固体核磁共振谱学可以用于一系列简单氧化物和沸石等催化剂的结构研究。近年来, 随着双旋转(DOR)、动态角旋转(DAS)、多量子魔角旋转(MQMAS)以及卫星跃迁魔角旋转(STMAS)等新技术的发展, 能够消除二阶四极耦合作用带来的谱线展宽, 显著提升谱图分辨率。而诸如交叉极化(CP)和旋转回波双共振(REDDOR)技术, 已经能用于探索氧与其它原子核空间相关方面的信息, 成为研究催化剂相关作用的基础。本文综述了氧化物及相关催化剂 ^{17}O 固体核磁共振谱学研究的新进展。

^{17}O 核磁共振谱学用于简单氧化物催化剂的结构研究, 已经能够区分催化剂结构中不同晶相以及不同结晶学位点的氧物种, 而 $^1\text{H} \rightarrow ^{17}\text{O}$ 双共振实验也能用于选择表面羟基物种。对纳米氧化物结构的近期研究表明, ^{17}O 核磁共振能将纳米氧化铈材料表面第1、2、3层、表面羟基、与氧空位靠近的氧物种与“体相”氧物种区分开来; 此外借助 ^{17}O -水和纳米氧化物作用, 实现表面选择标记, 为进一步探索催化剂结构和催化机理提供了新的可能。对于复合氧化物和负载催化剂, ^{17}O 核磁共振谱学能够有效研究与催化性能最为相关的界面结构。

在重要的氧化物催化材料沸石的研究中, ^{17}O 核磁共振也发挥了巨大作用。借助高分辨率 ^{17}O 核磁共振方法, 能够区分沸石中Si-O-Si和Si-O-Al物种, 在一部分沸石中还能将不同结晶学位位置的T-O-T物种区分开来, 并观测到天然沸石中违反Lowenstein规则, 出现Al-O-Al物种的情况。借助双共振实验能够对与催化活性最为相关的B酸位Si-O(H)-Al结构和酸性进行研究, 这一方法与探针分子相结合, 已经能够对沸石和小分子的相互作用进行研究, 提供吸附过程的重要信息。

包括杂多酸和层状双氢氧化物在内的重要含氧催化材料也能够借助 ^{17}O 固体核磁共振进行局域结构和相互作用的研究。

随着表面选择标记和动态核极化等选择表面研究的 ^{17}O 核磁共振技术的发展, 我们能实现更为高效的表面结构的 ^{17}O 核磁共振观测, 这一谱学方法将提供更多有关含氧催化剂和外来物种相互作用的信息, 为研究氧化物催化剂及其催化应用提供新的策略。

关键词: 氧-17; 固体核磁共振; 催化剂; 氧化物; 氢氧化物

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*通讯联系人. 电话: (025)83686793; 传真: (025)83686251; 电子邮箱: luming@nju.edu.cn

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