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Progress in development and application of solid-state NMR for solid acid catalysis

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ABSTRACT

Solid acid catalysts have been widely used in petrochemical industry and their catalytic activities are normally dictated by their acidities. Unlike conventional acidity characterization techniques such as titration, infrared, or temperature-programmed desorption, detailed acid features of solid acids, such as type, distribution, concentration, and strength of acid sites may be attained by advanced methods involving pertinent probe molecules and state-of-the-art solid-state nuclear magnetic resonance (SSNMR) techniques, i.e. double resonance and two-dimensional correlation spectroscopies. In addition, in situ solid-state NMR method is capable of probing the guest/host properties of the reactant at the active centers of the catalysts as well as the intermediate species formed during conversion. It provides direct experimental evidence for exploring the mechanism of catalytic reaction. In this report, the fundamental theory and the recent developments in solid-state NMR are reviewed with specific focus on relevant applications in structure and acidity characterization of solid acid catalysts and catalytic mechanisms.

1. Introduction

Catalytic materials have been widely used in the chemical industry, such as petroleum, coal chemical processing, pharmaceutical industry, fine chemicals, and environmental protection areas. In chemical industry, more than 80% reactions are catalytic processing [1], in which acid catalysts have been widely applied and well-studied. In petrochemical industry, most catalysts are liquid acid catalysts, such as sulfuric acid and hydrofluoric acid. However, the pollution produced during the processing and operation of these liquid acid catalysts has been of concern to the international community. In recent years, with the increasingly stringent environmental regulations, researchers are stepping up efforts to develop environmentally friendly solid acid catalysts to replace the traditional liquid acid catalysts. Zeolites, one type of the solid acid catalysts, have been applied extensively in industry.

Understanding the acidic properties of the catalysts is very

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helpful to explore the catalytic mechanism, modify catalysts as well as design improved solid acid catalyst. Generally, the most important acid features include acid type, distribution, concentration, and strength of solid acids. Table 1 lists available techniques for solid acid characterization. Conventional methods, such as titration, IR spectroscopy (either by direct observation of the OH groups or with adsorption of basic probe molecules), and temperature-programmed desorption (TPD) have been widely used for acidity characterization of catalysts. As shown in Table 1, these methods have some advantages and disadvantages in characterizing the acidic features of catalysts (acid type, distribution, concentration, and acid strength). Taking IR with probe adsorption as an example, its basic principle is dependent on the different interactions between probe molecules and various types of acid sites, such as hydrogen bonding and coordination interaction, resulting in characteristic stretching vibrations. Pyridine, one of the most commonly used probe molecules, adsorbed on Brönsted acid sites appears to have distinct peak at 1540 cm^{-1}, while at 1455 cm^{-1} when it is adsorbed on Lewis acid sites [1]. Thus, the IR with probe adsorption method can effectively distinguish between Brönsted and Lewis acid sites. However, it is also noteworthy that, since the absorption peak intensity and respective extinction coefficient are different when probe molecules adsorb on various acid sites, it is difficult to get quantitative information about the acid concentration by this technique.

With more than ten years' experience, we found there are several advantages using high-resolution solid-state nuclear magnetic resonance (SSNMR) to characterize the acidity of solid catalysts, including identification at atomic level, high resolution, and quantitative capability etc. [2]. As shown in Table 1, compared with the conventional characterization methods, state-of-the-art SSNMR techniques, such as double resonance and two-dimensional correlation spectroscopies, combined with advanced probe molecule technology can be applied to characterize the acid type, distribution, concentration, and acid strength of solid acids, which will help us to understand in more details about the acidic features of catalysts. In this review, we introduce the fundamental theory of solid-state NMR as well as the relevant applications in structure and acidity characterization of solid acid catalysts, to illustrate the strategy and progress of the in situ SSNMR applications in the reaction mechanism and catalyst structure-activity relationship.

2. Basic theory of solid-state NMR (SSNMR)

In NMR spectroscopy, when a nucleus with a non-zero spin quantum number ($I \neq 0$) is placed in a magnetic field, the non-degenerate energy levels of spin states are separated, which is known as the Zeeman effect. Additionally, the energy levels are also perturbed by internal nuclear spin interactions, mainly including chemical shift, *J* coupling, dipolar coupling, and quadrupole interactions, which are associated with the chemical and structural environments around the nucleus. In solutions, the rapid Brownian motion of molecules typically leads to averaging anisotropic interactions, which broaden the resonance lines, into isotropic interactions, such as the isotropic chemical shift and *J* coupling terms. Hence, high-resolution spectra can be easily obtained in solution NMR. For solid samples, the slow molecular motions cannot average the anisotropic terms to zero. Thus, NMR signals of powder samples normally exhibit broad resonance lines, which result in the low-resolution characteristics and the difficulties to distinguish and assign all the non-equivalent nuclei. Therefore, effectively designing and applying various SSNMR techniques to suppress or manipulate the anisotropic terms is an important strategy to achieve high-resolution SSNMR spectra, which is essential for exploring chemical and structural information of materials at the atomic/molecular level.

2.1. Internal nuclear spin interactions in solids

2.1.1. Chemical shift

Due to the existence of electron cloud around a nucleus, the effective magnetic field experienced by the nucleus spin is influenced by the distribution of surrounding electrons. Chemical shift describes the shielding effect of the electrons on the nucleus. The corresponding Hamiltonian for the chemical shift term can be written as:

$$\hat{H}_{CS} = \omega_0[\delta_{iso} + \frac{1}{2}\delta_{aniso}(3\cos^2\theta_{CS} - 1 + \eta\sin^2\theta_{CS}\cos 2\phi_{CS})]\hat{I}_z \quad (1)$$

in which, δ_{iso} is the isotropic chemical shift, δ_{aniso} is the anisotropic parameter, η represents the asymmetric factor, θ_{CS} and ϕ_{CS} are the polar angles of the external magnetic field in chemical shift tensor. As the orientation of the molecules in the powder sample varies with respect to the external field, the anisotropy of the shielding effect results in various chemical shifts. As

Table 1
Comparison of available techniques for acidity characterization [2].

Method	Probe	Acid type		Acid distribution	Acid concentration	Acid strength
		Brönsted	Lewis			
Titration		+	+	−	+	+
TPD	NH_3	+	+	−	+	±
IR	hydroxyls	+	−	−	−	+
	pyridine	+	+	+	±	±
^{1}H NMR	hydroxyls	+	−	−	±	−
	pyridine-d_5	+	−	−	±	−
^{13}C NMR	2-^{13}C-acetone	−	−	−	−	+
^{31}P NMR	TMP	+	+	−	+ (B); − (L)	− (B); + (L)
	R_3PO	+	+	+	+ (B); + (L)	+ (B); + (L)

+: Superior; ±: Fair; −: Inferior; B: Brönsted acid; L: Lewis acid; TMP: trimethylphosphine; R_3PO: trialkylphosphine oxides.