

³¹P NMR Spectroscopy of Adsorbed Probe Molecules as a Tool for the Determination of the Acidity of Molecular Sieve Catalysts (A Review)

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Received April 28, 2021; revised May 11, 2021; accepted May 12, 2021

Abstract—The review analyzes the potential of ³¹P MAS NMR spectroscopy of adsorbed trisubstituted phosphines and phosphine oxides for the investigation of the acidic properties of molecular sieve catalysts. The main methodological approaches to identifying sites of different types are considered. The assignment of signals in the ³¹P MAS NMR spectra of methyl-, ethyl-, *n*-butyl-, and phenyl-substituted phosphines and their oxides adsorbed on zeolites of different structural types and other molecular sieves to Lewis and Brønsted acid sites is reported, and the potential of ³¹P MAS NMR spectroscopy as a tool for the determination of the strength of these sites and their amount is analyzed. It is shown that varying the size of the substituent allows assessment of the localization and accessibility of acid sites in zeolites.

Keywords: zeolites, probe molecules, ³¹P MAS NMR spectroscopy, trisubstituted phosphines, trisubstituted phosphine oxides

DOI: 10.1134/S0965544121080107

Targeted control of the catalytic properties of molecular sieve materials and the creation on their basis of highly efficient catalysts requires knowledge of their acidic properties responsible for the catalytic activity of petrochemical and gaseous processes [1]. Therefore, at present, much attention is paid to the development of methods for assessing the type of acid sites and their strength, concentration, and accessibility for various substrates [2]. To determine all these characteristics is an important task for predicting the activity of molecular sieve catalysts.

The main methods for studying the acidity of zeolites include titration with indicators, temperature-programmed desorption of ammonia (NH₃-TPD), and infrared spectroscopy (IR) of adsorbed probe molecules [3]. Although the indicator titration of active sites in aprotic solvents is a simple and classical method for the quantification of the acid–base properties of solids [4], it has many disadvantages. First, this method does not allow classifying acid sites in terms of their nature and strength

and, second, the ability of quite large indicator molecules to penetrate into the zeolite framework is limited for steric reasons, which, in turn, leads to significant errors in the quantitative analysis [5]. The NH₃-TPD method makes it possible to estimate the number and strength of acid sites but does not provide information on their nature. Infrared spectroscopy of adsorbed pyridine and its substituted homologues provides information on the nature of active sites and their accessibility but not always allows reliable estimation of their amount. Thus, all the currently available methods are not free of limitations.

Over the past years, increasing attention has been paid to the MAS NMR spectroscopy of adsorbed organophosphorus bases [6]. The method consists in recording the ³¹P MAS NMR spectra of adsorbed probe molecules. The positions of signals in the spectrum provide information on the type and strength of acid sites, and the intensity of the signals allows estimation of the number of the sites. By varying the size of the probe

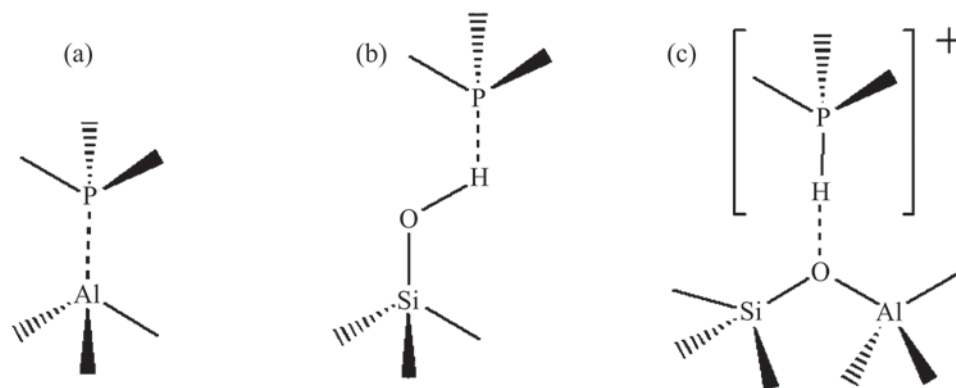


Fig. 1. Interaction of trimethylphosphine with different acid sites of zeolites: (a) Lewis acid site, (b) silanol group, and (c) Brønsted acid site.

molecule one can get information on the accessibility of the acid sites for various substrates.

In this review, we consider the main types of probes used to study the acidic properties of molecular sieves by the ^{31}P MAS NMR method, analyze the advantages and disadvantages, and give examples of their use to determine the type, strength, availability, and number of acid sites in molecular sieves of different types.

1. ^{31}P MAS NMR SPECTROSCOPY OF ADSORBED SUBSTITUTED PHOSPHINES R_3P

Alkyl- and aryl-substituted tertiary phosphines of the general formula R_3P are widely used as phosphorus-containing probe molecules for MAS NMR spectroscopy. Due to the presence of the lone electron pair, the phosphine molecule can interact with the acid sites of zeolites and zeolite-like materials. Figure 1, using the example of trimethylphosphine (Me_3P), schematically presents the possible variants of such an interaction with Lewis acid sites (Fig. 1a), silanol groups (Fig. 1b), and bridging hydroxyl groups of Brønsted acid sites (Fig. 1c).

The first use of tertiary phosphines as probe molecules for studying the acid properties of zeolites by means of solid-state NMR spectroscopy dates back to 1980s [7]. Lunsford and co-workers studied the acid properties of faujasite by trimethylphosphine adsorption and showed that trialkylphosphines hold promise as molecular probes. Later this approach became widespread. Various probe molecules were studied on different structural types of zeolites, and the spectral signals were assigned to acid sites of different types, strengths, and localization.

1.1. Identification of Acid Sites of Different Types

The primary task in the ^{31}P MAS NMR spectroscopy of adsorbed phosphine molecules was to assign the spectral signals to acid sites of different types. Several approaches have been proposed for this purpose. The main direction was the use of model connections. To determine the chemical shifts of the signals of probes adsorbed on Lewis acid sites (LAS), we used such models as aluminum oxides [8–11], aluminosilicates [9, 12–14], zinc oxide [15], free and sulfated zirconium and titanium oxides [11, 16–17], as well as aluminum chloride [8]. Heteropoly acids (HPA) [18] and concentrated HCl [19] were used to assign the signals of phosphine molecules adsorbed on Brønsted acid sites (BAS).

Figure 2 provides a schematic representation of the ranges of the ^{31}P MAS NMR signals of adsorbed Me_3P , depicted based on the data in [8–11, 16, 18, 20–21]. As seen from the figure, the signals of trimethylphosphine interacting with BAS span the range from -3 to -5 ppm, and the signals corresponding to trimethylphosphine adsorbed on LAS range from -35 to -61 ppm. It should be noted that the region of signals assigned to LAS overlaps with the region of signals corresponding to physical adsorption of probes. This complicates the interpretation of spectral data and requires the use of special approaches for reliable signal assignment.

To clarify the assignment of signals to physisorbed phosphine, Hu et al. [19] made use of high-temperature vacuum treatment of a sample with adsorbed phosphine. In this case, the partial or complete disappearance of the signal was considered as evidence for its assignment to the

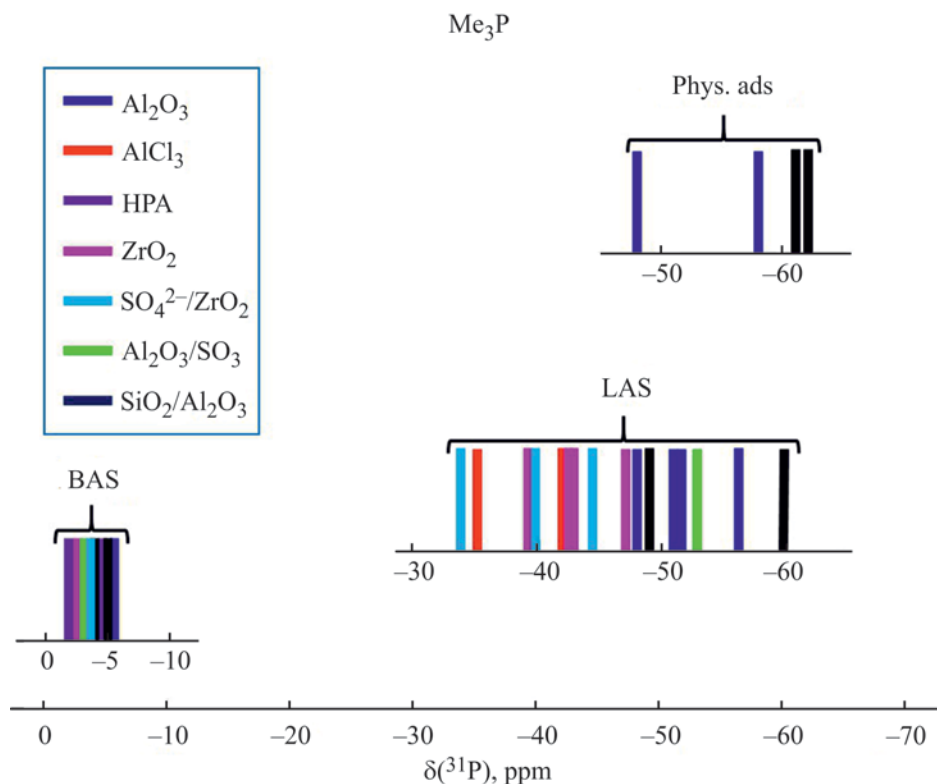


Fig. 2. Assignment of signals in the ^{31}P MAS NMR spectra of trimethylphosphine adsorbed on various model compounds [8–11, 16, 18, 20, 21].

physisorbed probe. To clarify the assignment of signals to LAS and BAS, various pulse sequences are used. In the case of BAS, the ^{31}P – ^1H coupling is confirmed by recording proton-decoupled and proton-coupled spectra [22], or by using pulse sequences to transfer polarization from ^1H to ^{31}P [23]. In the case of LAS, the ^{31}P – ^{27}Al coupling is confirmed using the TRAPDOR pulse sequence [23], or by using fields of different strengths, which leads to a change in the width of the ^{31}P signal due to the nuclear quadrupole moment of ^{27}Al [9].

It should be noted that another difficulty in interpreting the ^{31}P MAS NMR spectra of adsorbed phosphine molecules is their ability to undergo oxidation. In this case, the signals of adsorbed phosphine oxides that appear in the spectra may overlap with the signals of phosphines. To avoid oxidation, special sample preparation in an inert atmosphere should be performed [13].

Thus, as follows from an analysis of published data, at present a great body of evidence is available, which makes it possible to assign signals in the ^{31}P MAS NMR spectra

of adsorbed phosphine molecules to acid sites of different types. In this case, the main difficulties in interpreting the spectral data are associated with partial overlap of the signals of physisorbed phosphines with the signals of physisorbed phosphines with the signals of phosphines adsorbed on LAS, as well as with the possibility of oxidation of this class of probe molecules.

1.2. Adsorption of $R_3\text{P}$ Molecules on Molecular Sieves of Different Structural Types and Compositions by ^{31}P NMR MAS Spectroscopy

Table 1 lists the results of studies of zeolite and zeolite-like materials by the ^{31}P MAS NMR spectroscopy of adsorbed substituted phosphines. Most effort was focused on the acidity of faujasite-type zeolites (H–Y). In addition, zeolites of the structural types MFI, BEA, MOR, MWW, and TUN, as well as mesoporous molecular sieves MCM-41 and SBA-15 were studied. These studies used two types of probes: Me_3P and Ph_3P .

The H-forms of freshly prepared zeolites, calcined at moderate temperatures, generally exhibit Brønsted

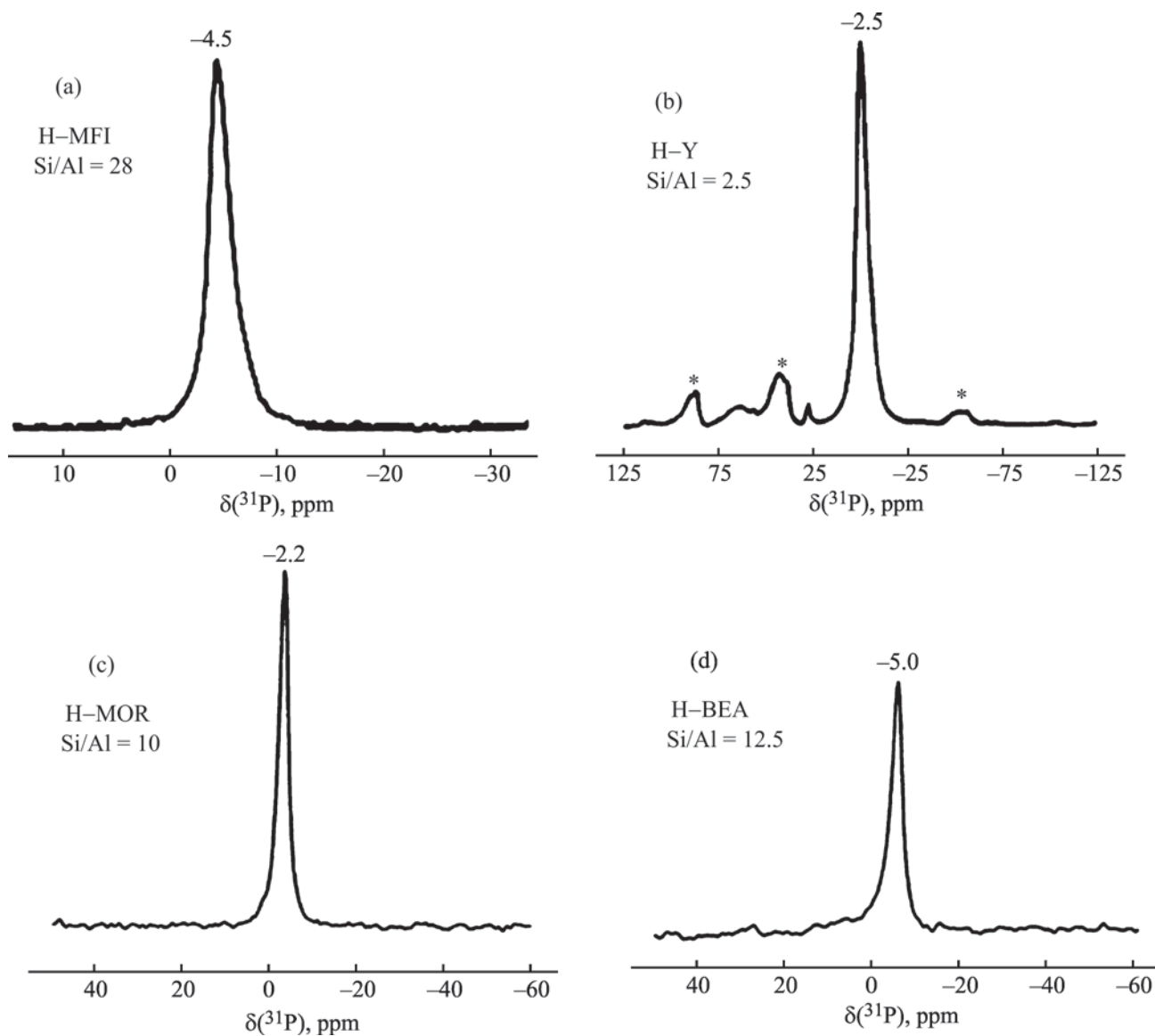


Fig. 3. ^{31}P MAS NMR spectra of trimethylphosphine adsorbed on zeolites of different structural types: (a) MFI [27], (b) FAU (Y zeolite) [8], (c) MOR [22], and (d) BEA [22].

acidity only. The typical ^{31}P MAS NMR spectra of trimethylphosphine adsorbed on the H-forms of zeolites of different structural types are shown in Fig. 3. All the spectra contain a single peak assignable to Brønsted acid sites. The position of the peak depends on the type of the zeolite: the chemical shifts of low-silicon zeolites (H-Y, MOR) fall in the range from -2 to -2.5 ppm, and those of high-silicon zeolites (MFI, BEA), in the range -4.5 to -5 ppm. This shift can be associated with both the structural features of and different molar Si/Al ratios in the zeolites.

It should be noted that, according to DFT calculations, the positions of signals corresponding to BAS are only slightly dependent on the strength of the Brønsted acid site (Fig. 4) [6]. The signals of charge-transfer complexes fall in a very narrow range (from -2 to -5 ppm), which agrees with the experimental data obtained on zeolites and model compounds (Fig. 2, Table 1). These findings imply that the strength of BAS is impossible to determine unambiguously and very accurately using tertiary organic phosphines as probe molecules.

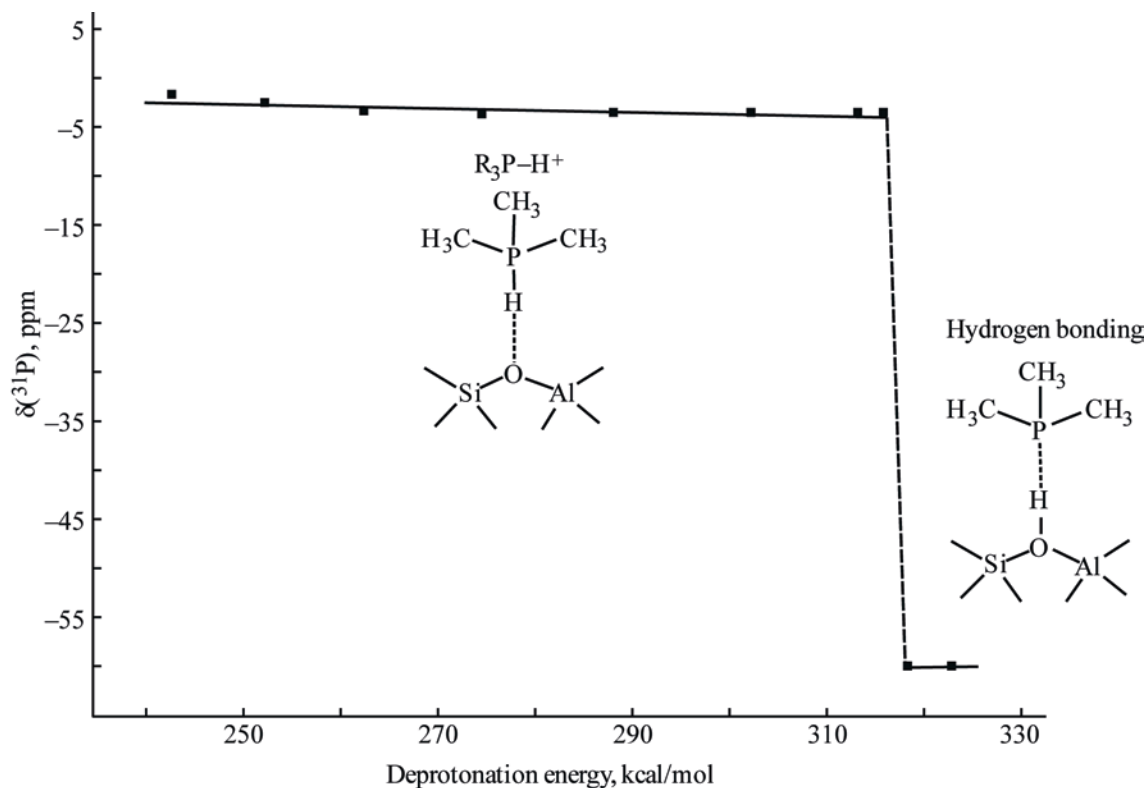


Fig. 4. Dependence of the chemical shift of the signal of the protonated trimethylphosphine complex on a Brønsted acid site on the deprotonation energy [6].

Lewis acid sites are formed on zeolites as a result of either dehydroxylation under thermal treatment or dealumination. The ^{31}P MAS NMR spectra of trimethylphosphine adsorbed on H-Y zeolites calcined at different temperatures [8] are shown in Fig. 5. When the calcination temperatures were 500°C and higher, the ^{31}P MAS NMR spectra displayed additional signals at -32, -44, -47, -50, -54, and -58 ppm, which, according to [8], belonged to Me_3P adsorbed on Lewis acid sites.

The same picture is observed in the case of the hydrothermal dealumination of MFI zeolite. Zhang et al. [27] removed aluminum from the MFI zeolite structure by steam treatment at different temperatures. The dealuminated zeolite was then allowed to adsorb Me_3P , after which the ^{31}P MAS NMR spectra of the resulting samples were measured. The spectra of Me_3P adsorbed on the initial zeolite contained signals at -4.5 and -62.1 ppm, assigned to Me_3P complexes with BAS and physisorbed Me_3P , respectively (Fig. 6). After dealumination, the first signal assigned to BAS lost intensity, and, therewith, this intensity loss was the stronger, the higher was the dealumination temperature. After dealumination the

intensity of the signal of trimethylphosphine adsorbed on LAS increased, which is consistent with the appearance in the samples of extralattice aluminum detected by ^{27}Al MAS NMR.

As seen from Table 1, the signals of trimethylphosphine adsorbed on LAS characteristically appear at -32 to -60 ppm. These signals frequently overlap with each other, as well as with signals of physisorbed Me_3P molecules (-59 to -67 ppm), which agrees with data for model compounds (Fig. 2). According to the quantum-chemical calculations performed by Chu et al. [32] for several types of LAS, the position of signals of trimethylphosphine adsorbed on different Lewis acid sites is linearly related to the bond energy between Me_3P and an atom (B, Al, and Ti) in LAS (Fig. 7). This result suggests that the use of tertiary organic phosphines as probe molecules makes it possible to estimate the strength of Lewis acid sites.

1.3. Determination of the Localization and Accessibility of Acid Sites

Molecular sieves are effective catalysts for a wide range of reactions differing in the size of reagents and

Table 1. Assignment of signals in the ^{31}P MAS NMR spectra of phosphines adsorbed on molecular sieves of different structural types

Probe	Sample	Assignment	$\delta(^{31}\text{P})$, ppm	References	
Me_3P	H–Y	BAS	–2 to –6	[7, 8, 23–25]	
		LAS	–32, –44 to –58	[8]	
		Physisorbed	–60, –67	[7, 8, 23]	
	H–Y, dealuminated	BAS	–4.9	[24]	
		H–MFI	BAS	–3.5 to –4.5	[24, 26, 27]
			LAS	–57, –60	[27]
	Ti–MFI	Physisorbed	–59.4 to –62.2	[26, 27]	
		BAS	–3.9 to –4.3	[28, 29]	
		LAS	–33.7	[29]	
	Al–MCM-41	Physisorbed	–58.5		
		BAS	–4	[30]	
		Physisorbed	–59		
	H–MOR	BAS	–2.2	[22]	
		H–BEA		–5	
				–4	[19]
Al–SBA-15		Physisorbed	–56		
			–4		
Ph_3P	MWW	BAS	10 to 14.8	[13, 31]	
		Physisorbed	–4.6	[31]	
			–6	[13]	
	MFI	Physisorbed	–6		
			–6		
	TUN	BAS	7		
			–6		
	MFI, alkali-treated	Physisorbed	–6		
		BAS	7		
	TUN, alkali-treated	Physisorbed	–6		
		BAS	7		

products. Therefore, an important characteristic of these systems is the localization of acid sites in their porous structure and the availability of acid sites for substrates of different sizes. A promising approach to determine these parameters consists in the use of molecular probes of different sizes.

A molecule of trimethylphosphine has the smallest size (~ 0.55 nm) [8] and can penetrate into the porous system of wide- and medium-pore zeolites, such as H–Y, H–MOR, H–BEA, and H–MFI [8, 22, 23, 27]. By contrast, such large molecules as Ph_3P (1.17×0.71 nm [33]) should not penetrate into the porous structure of zeolites, and, therefore, these molecules are suitable only

for studying the acidity of the external surface of crystals or acid sites in mesopores formed after modification of zeolites by different methods.

Wang et al. [31] performed DFT calculations of the interaction of triphenylphosphine with MWW zeolite. The results showed that the Ph_3P molecule is too large to penetrate into the zeolite pores and, therefore, can interact only with acid sites located on the external surface of crystals, preferably in the mouths of 12-membered pores.

Rieg et al. [13] studied the accessibility of acid sites in microporous TUN and MFI zeolites, as well as in the hierarchically porous TUN/h и MFI/h zeolites prepared by treatment TUN and MFI zeolites with alkali followed

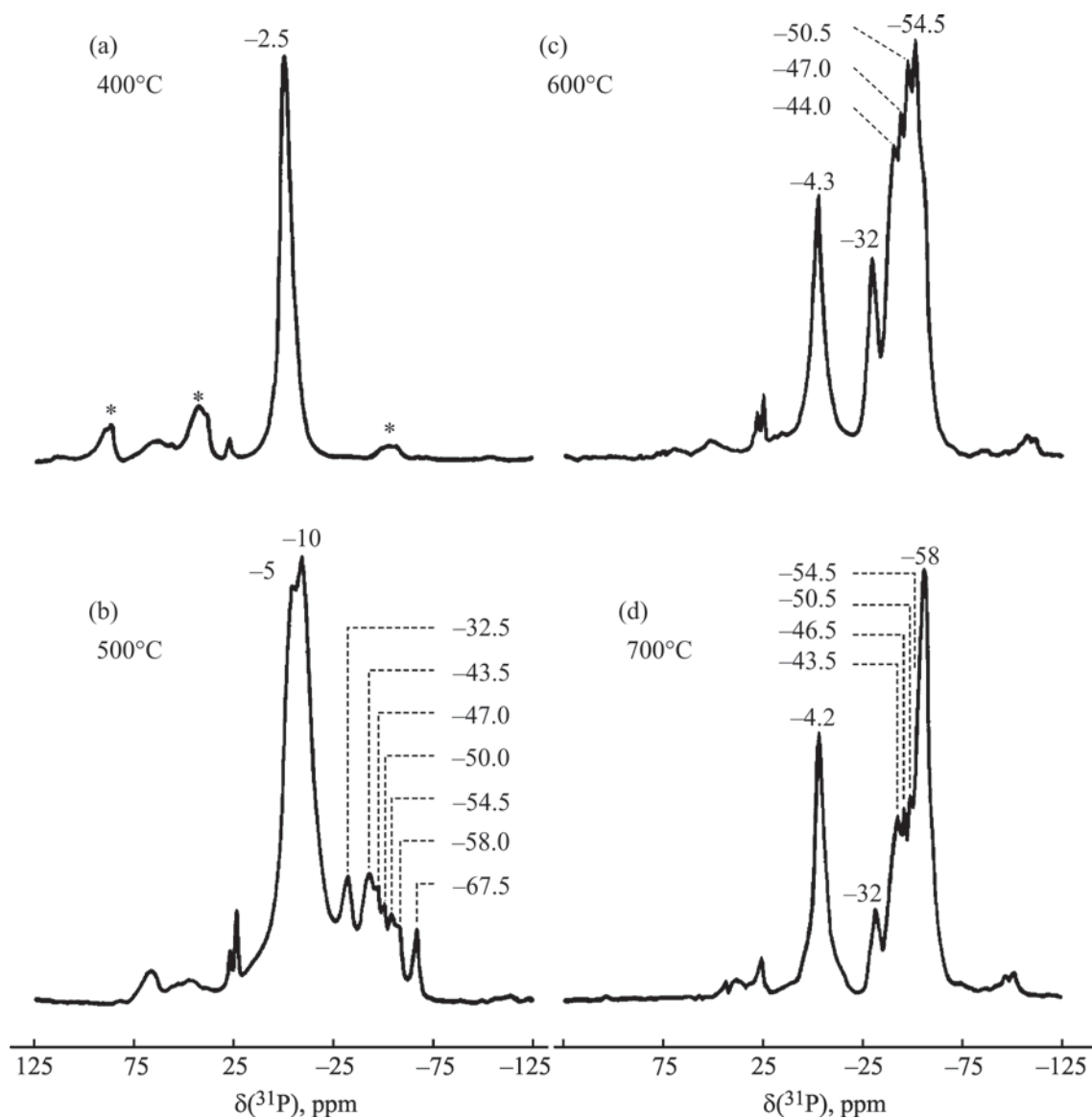


Fig. 5. ^{31}P MAS NMR spectra of trimethylphosphine adsorbed on H-Y zeolites calcined at different temperatures [8].

by washing with acid. Triphenylphosphine was used as the probe (Fig. 8). The signal at 7 ppm was assigned to the complexes of Ph_3P with Brønsted acid sites, and the signal at -6 ppm, to physisorbed Ph_3P molecules. The resulting data allowed the authors of [13] to conclude that the external surface of the starting MFI zeolite, unlike what is observed with TUN, is not very acidic. The generation of mesopores by treatment with alkali and acid strongly facilitates access to acid sites.

Thus, the use of tertiary phosphines with bulky organic substituents makes it possible to determine the number

of acid sites on the external surface of crystals and in mesopores.

1.4. Quantitative Determination of Acid Sites

It is also very important in studying the acidity of zeolites to determine the amount of acid sites of different types. Quantitative data are needed not only for direct comparison of catalysts, but also for predicting their catalytic activity, and, as a consequence, targeted synthesis of highly active and selective catalysts for specific processes. However, this problem is usually quite difficult to solve.

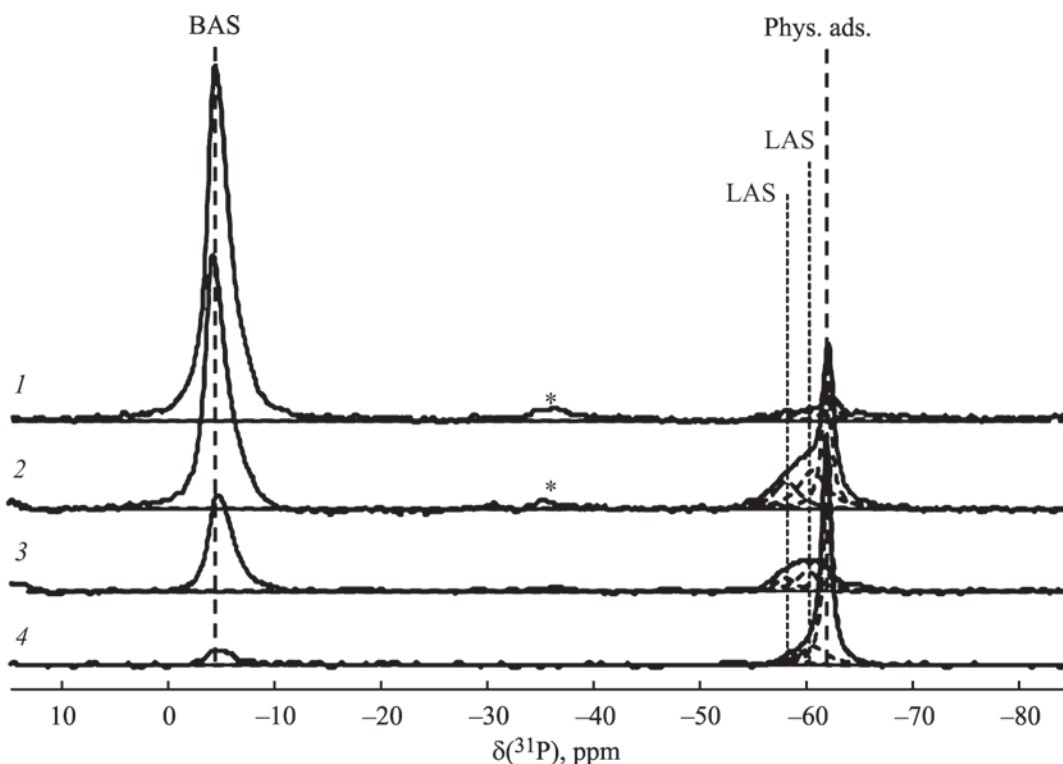


Fig. 6. ^{31}P MAS NMR spectra of Me_3P adsorbed on MFI zeolite before and after dealumination at different temperatures: (1) before hydrothermal dealumination and after delumination at (2) 400°C, (3) 500°C, and (4) 700°C [27].

There are two main approaches to determining the number of acid sites: 1) normalization of the spectrum intensity to the total amount of phosphorus adsorbed on the sample and 2) the use of an external standard when recording the spectra. The adsorbed amount of phosphorus is set during sample preparation or is

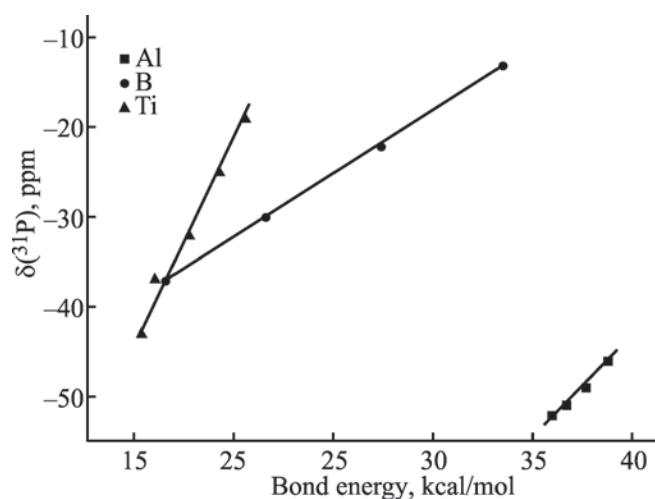


Fig. 7. Dependence of the chemical shifts of the ^{31}P MAS NMR signals of trimethylphosphine adsorbed on Lewis acid sites on the bond energy [32].

determined by elemental analysis [9]. Diammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ [19, 22] or VPI-5 zeolite with the VFI structure [13, 34] are usually used as external standards.

Sample preparation is the source of the largest errors in estimation of the amount of acid sites. This is especially true for substituted phosphines with a high molar mass, which are solids. In this case, phosphines should be either heated at high temperatures until evaporation, which does not guarantee their uniform adsorption on all acid sites, or applied from a solution, which is often accompanied by oxidation of the probe. This leads to large errors in determining the number of acid sites.

It is worth noting that, according to Baltusis et al. [9], the area of the signal assigned to LAS is much affected by exchange processes between physisorbed trimethylphosphine molecules and those adsorbed on LAS. These authors concluded that quantitative analysis is feasible only for BAS.

Thus, analysis of the literature data allows us to conclude that substituted phosphines R_3P can be used as reliable probes for determining the number of BAS. The ^{31}P MAS NMR signals of the protonated forms

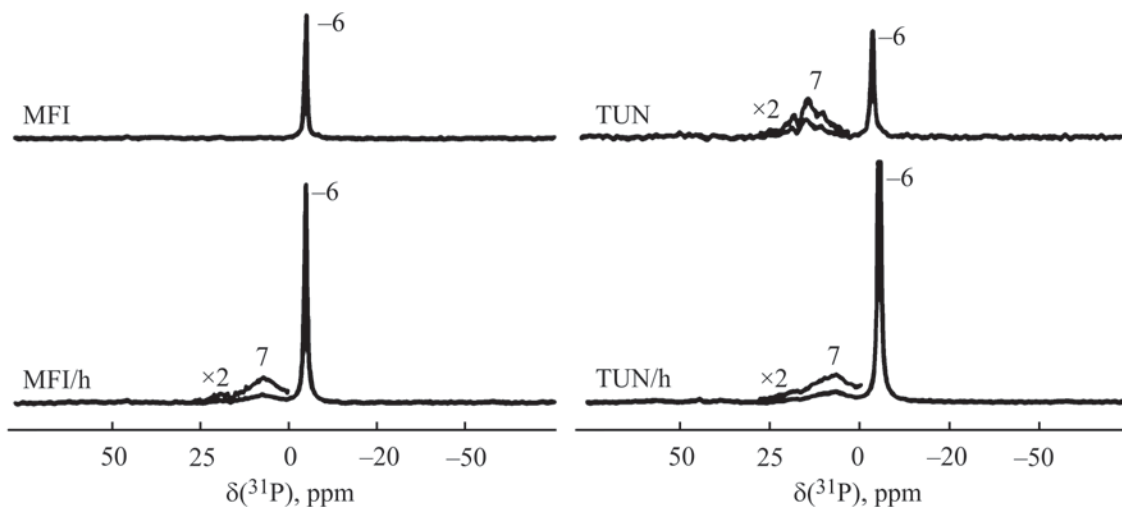


Fig. 8. ³¹P MAS NMR spectra of triphenylphosphine adsorbed on MFI, MFI/h, TUN, and TUN/h [13].

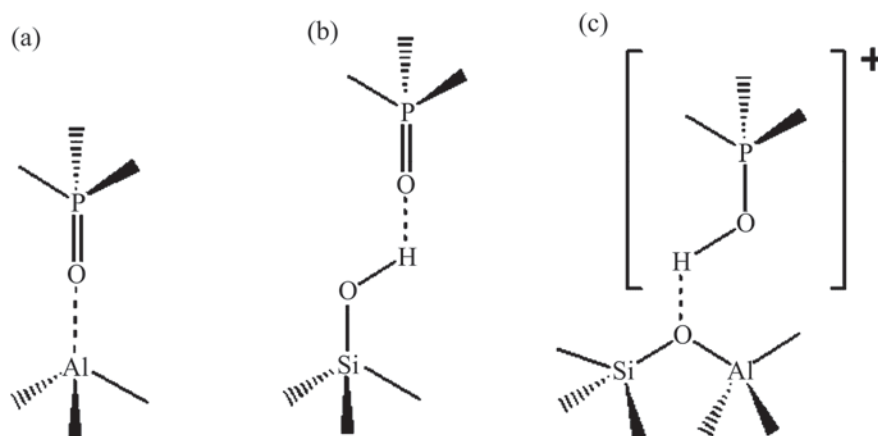


Fig. 9. Interaction of trimethylphosphine oxide with different acid sites of zeolites: (a) Lewis acid site, (b) silanol group, and (c) Brønsted acid site.

of substituted phosphines do not overlap both with physisorbed molecules and with those adsorbed on LAS. Varying the size of the substituent on the phosphorus atom makes it possible to determine both the total acid sites and the acid sites of the external surface of the supports and catalysts. At the same time, such probes are unsuitable for determining the strength of BAS because of the very narrow range of the chemical shifts of their NMR signals. A different picture is observed with LAS. In this case, the use of phosphines as probe molecules allows one to determine the strength of LAS, but the situation is complicated by the fact the signals of phosphines adsorbed on LAS overlap with those of physisorbed

molecules, thereby making difficult the quantification of LAS. Another disadvantage of substituted phosphines is their tendency for oxidation during sample preparation.

2. ³¹P MAS NMR OF ADSORBED TRISUBSTITUTED PHOSPHINE OXIDES R₃PO

The use of tertiary alkyl- or arylphosphine oxides as probe molecules for acidity studies offers a number of advantages over the use of phosphines: these compounds are not oxidized during sample preparation and they are more convenient in operation and more sensitive to the type and strength of Brønsted acid sites. Figure 9, on an example of trimethylphosphine oxide

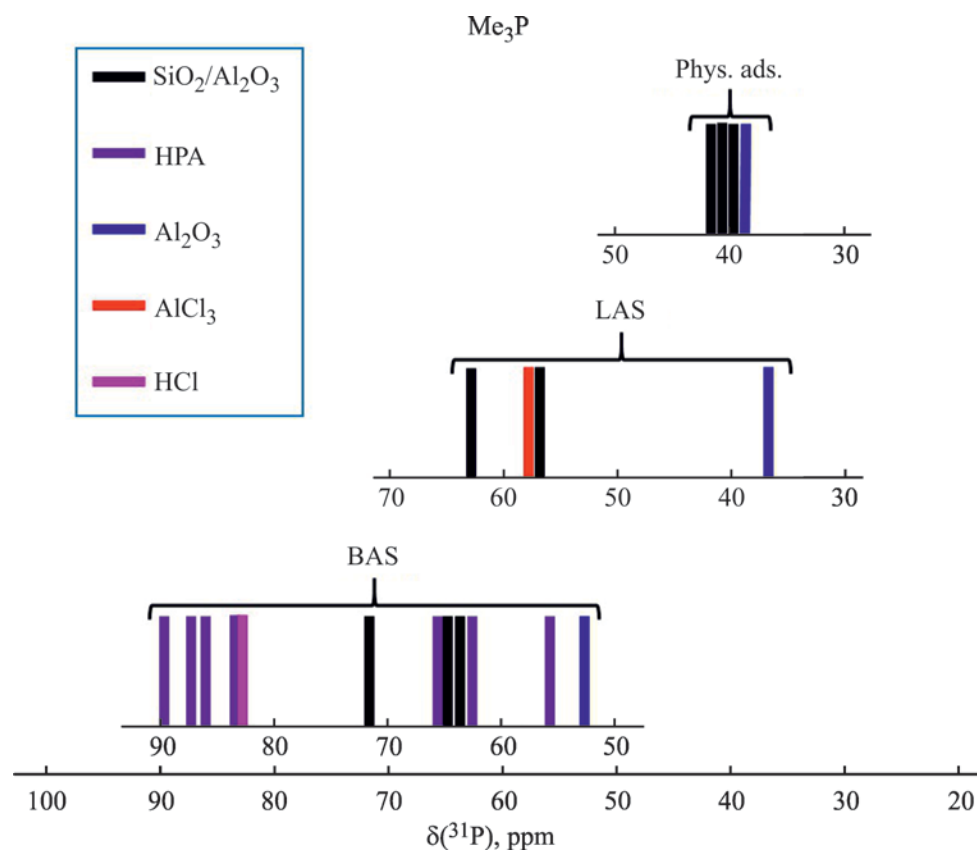


Fig. 10. Assignment of signals in the ^{31}P MAS NMR spectra of trimethylphosphine oxide adsorbed on different model compounds [35, 36, 38, 39].

(Me_3PO), schematically shows the ways of interaction of trisubstituted phosphine oxides with (a) Lewis acid sites, (b) silanol groups, and (c) Brønsted bridging acid sites.

The most common molecular probe for studying the acid properties of zeolites is trimethylphosphine oxide (Me_3PO). Along with the latter, oxides of triethylphosphine (Et_3PO), tri-*n*-butylphosphine (*n*- Bu_3PO), tri-*n*-octylphosphine (*n*- Oct_3PO), and triphenylphosphine (Ph_3PO) are used. At present, a great body of data has been accumulated on the use of these probe molecules for studying zeolites and zeolite-like materials of different structural types, the spectral signals have been assigned to acid sites of different natures, and methodological approaches have been developed for determining the number, strength, and localization of acid sites of different types.

2.1. Identification of Acid Sites of Different Types by ^{31}P MAS NMR Spectroscopy of Adsorbed R_3PO

Like with phosphines, the ^{31}P MAS NMR spectra of adsorbed substituted phosphine oxides were assigned with the help of model compounds. The chemical shifts of the

signals of free or physisorbed probes were determined in the solid-phase spectra of phosphine oxides, as well as in the spectra of solutions of phosphine oxides in different solvents [35]. The signals of R_3PO bound to LAS were identified using as model compounds AlCl_3 [36], $\gamma\text{-Al}_2\text{O}_3$ [35, 37], and aluminosilicates [35]. Heteropoly acids (HPA) [38] and HCl [35] were used as model compounds to identify the signals of R_3PO adsorbed on Brønsted acid sites.

Figure 10 schematically presents the chemical shifts of the signals assigned to BAS and LAS, as well as to physisorbed probe in the ^{31}P MAS NMR spectra of Me_3PO adsorbed on different model compounds. As seen from the figure, the signals of Me_3PO interacting with BAS and LAS are characteristically observed in the ranges 53–90 and 37–65 ppm, respectively. The signals of the free and physisorbed probe span the range 39–42 ppm.

It should be noted that the chemical shifts of the signals corresponding to molecules adsorbed on BAS span a much wider range for R_3PO (Fig. 10) than for R_3P (Fig. 2). This fact suggests that R_3PO is a more sensitive

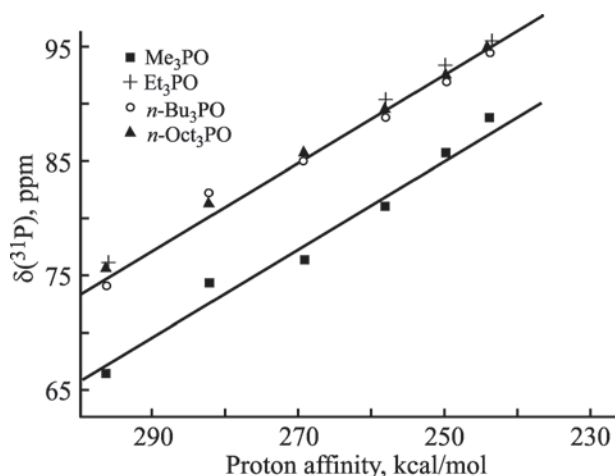


Fig. 11. Dependence of the chemical shifts of the signals of R₃PO on proton affinity [40].

probe to the nearest environment of the proton center, and, therefore, can more finely distinguish between BAS of different natures and strengths. Quantum-chemical calculations by the DFT method [40] showed that the

chemical shift of Me₃PO varies in parallel with the proton affinity of the adsorbent as a measure of the strength of BAS (Fig. 11) and can vary over a wide range from 65 to 90 ppm, which is in good agreement with the experimental data in Fig. 10.

The same tendency is observed with other probes, such as Et₃PO, *n*-Bu₃PO, and *n*-Oct₃PO, the chemical shift of which, too, varies over a wide range (75 to 95 ppm) with the proton affinity of the adsorbent (Fig. 11). Therefore, the calculated chemical shifts of alkylphosphine oxides with a longer alkyl hydrocarbon chain differ from those of Me₃PO by ~8 ppm, which well agrees with the experimental data (Fig. 12) [40].

Another important feature of the ³¹P MAS NMR spectra of adsorbed R₃PO is the overlapping ranges of the BAS and LAS regions, as well as the LAS and probe physisorption regions (Fig. 10). It complicates interpretation of spectral data and requires special approaches to assign the signals.

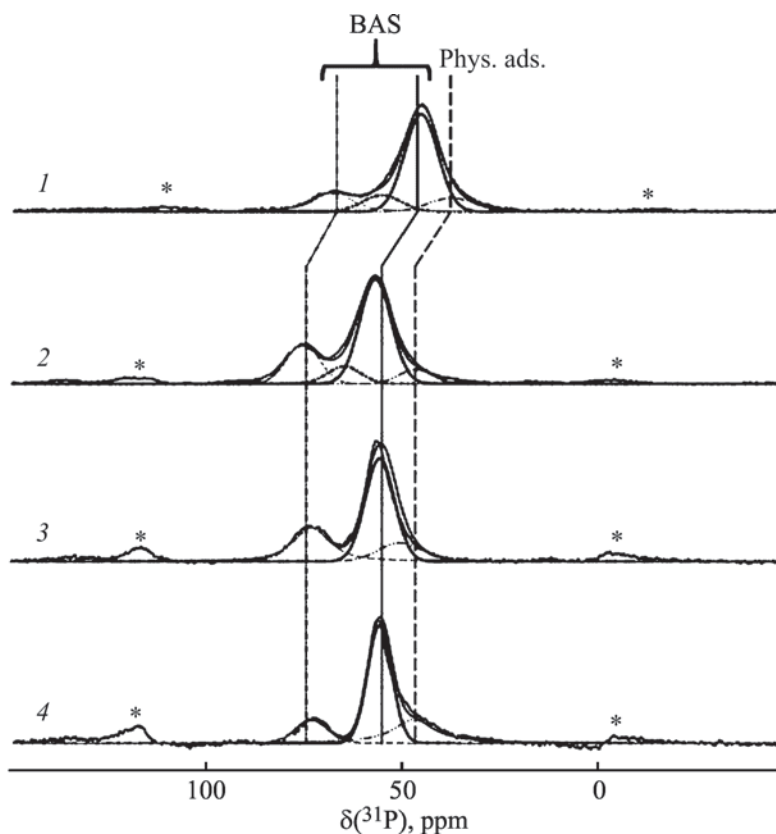


Fig. 12. ³¹P MAS NMR spectra of (1) Me₃PO, (2) Et₃PO, (3) *n*-Bu₃PO, and (4) *n*-Oct₃PO, adsorbed on the mesoporous support MCM-41 [40].

To clarify the assignment of signals of R_3PO adsorbed on LAS and BAS, the authors of [26, 35, 41] made use of the co-adsorption of water molecules. It was assumed that water molecules replace the R_3PO molecules bound to LAS, which makes it possible to identify such acid sites by a decrease in the intensity of the corresponding signals. However, the interaction of LAS with water may result in the formation of “new” Brønsted acid sites, thereby complicating spectral assignment.

Another, more reliable approach involves selective poisoning of LAS or BAS. For example, to poison Brønsted acid sites, Zhao et al. [42] used 2,6-dimethylquinoline, and to remove extralattice aluminum responsible for Lewis acidity, treatment with HCl. Furthermore, the signals of R_3PO adsorbed on LAS and BAS are identified by different pulse sequences: 1H to ^{31}P cross-polarization and ^{27}Al on-resonance irradiation (REDOR and TRAPDOR experiments) [43, 44].

To clarify the assignment of signals to physisorbed phosphine oxides, like with phosphines, an additional procedure of high-temperature vacuum treatment of samples with varied amounts of adsorbed substituted phosphine oxides is applied [43, 44].

Thus, the main advantage of phosphine oxides is their high sensitivity to the type and strength of Brønsted acid sites. However, the signals of phosphine oxides adsorbed on BAS and LAS not infrequently overlap, which requires the use of special approaches for reliable signal assignment.

2.2. Adsorption of R_3PO on Molecular Sieves of Different Structural Types and Compositions by ^{31}P MAS NMR Spectroscopy

Table 2 lists the data for zeolite and zeolite-like materials, obtained by the ^{31}P MAS NMR spectroscopy of adsorbed phosphine oxides. As seen from the table, the largest number of works is devoted to zeolites with the FAU (H–Y, USY, REH–Y) and MFI structures. Some data for MOR and BEA zeolites, as well as for mesoporous molecular sieves MCM-41 are also available. The probe molecules applied were Me_3PO , $n-Bu_3PO$, and Ph_3PO .

Analysis of the literature showed that the use of R_3PO as probes allows one to identify BAS of different types and gain detailed information on their strength. In certain cases, valuable data on Lewis acid sites can also be obtained. Using probes of different sizes makes it possible to assess the accessibility of BAS and LAS.

2.2.1. Study of Brønsted Acid Sites

Figure 13 presents the ^{31}P MAS NMR spectra of trimethylphosphine adsorbed on the H-forms of zeolites of different structural types [22, 26, 41].

The spectra of each zeolite contain several signals assigned to Me_3PO molecules adsorbed on Brønsted acid sites (range 50–100 ppm) and to physisorbed probe (30–50 ppm). The signals of Me_3PO interacting with BAS of the studied zeolites are observed in different spectral regions. The strongest signals fall in the following ranges, δ , ppm: 55–65 (H–Y), 58–77 (H–BEA), 63–75 (H–MFI), and 62–80 (H–MOR). From a comparison of these ranges we can rank the zeolites in the following series in terms of the strength of acid sites: H–Y < H–BEA \approx H–MFI < H–MOR. This series is in good agreement with the data of other methods, in particular, temperature-programmed desorption of toluene [51].

It should be noted that the results obtained with Me_3PO greatly differ from the results obtained with Me_3P for the same zeolite samples [22]. The spectra of adsorbed Me_3P contain only one signal (Fig. 2), whereas the spectra of Me_3PO allow identification of different Brønsted sites in the zeolite structure. The presence of several Brønsted sites in zeolites can be associated with their different localization, changes in their immediate environment, as well as the influence of extralattice fragments formed during synthesis or as a result of post-synthetic treatments.

Obenaus et al. [45] studied the effect of localization of BAS in the structure of Y zeolite on the position of signals in the ^{31}P MAS NMR spectra of adsorbed trimethylphosphine oxide (Fig. 13). Samples with different localizations of BAS in large and small cavities of the zeolite were obtained by varying the degree of ion exchange of Na^+ for H^+ in NaY zeolite. As known from the literature, at low degrees of exchange, proton centers are located mainly in large cavities of Y zeolite, and at high degrees of exchange they are also accommodated in the sodalite cavities [52, 53].

Figure 14 shows that, at low exchange rates, a signal at 66 ppm, corresponding to Me_3PO adsorbed on BAS in large cavities of Y zeolite, was predominantly observed in the spectrum. At higher degrees of ion exchange, a signal at 56 ppm related to Me_3PO interacting with BAS in small sodalite cavities appeared in the spectrum. These results made it possible to identify BAS with different localizations in the zeolite structure by analyzing the

Table 2. Assignment of the ³¹P MAS NMR signals of trisubstituted phosphine oxides adsorbed on molecular sieves of different structural types

Probe	Sample	Assignment	δ(³¹ P), ppm	References
Me ₃ PO	H-Y	BAS	55–78	[35, 37, 43, 45]
		LAS	37	[46]
		Silanol groups	40	[43]
			48	[45]
	USY	Free and/or physisorbed	39–44	[35, 45, 46]
		BAS	53–65	[35, 37, 46]
		LAS	37	[46]
	REH-Y ^a (RE = La, Ce)	Free and/or physisorbed	39–44	[35, 37, 46]
		BAS	53–70	[41]
		LAS	55, 78	
	H-MOR	Free and/or physisorbed	41, 49	
		BAS	50–86.4	[22, 47]
	H-BEA	Free and/or physisorbed	52.5	
		BAS	55–85	[22, 42, 48]
	H-MFI	LAS	49–65, 85	
		Free and/or physisorbed	31–46.5	
		BAS	53–92	[26, 48, 49]
	MCM-41	LAS	65, 84	[48]
Free and/or physisorbed		30–56	[26, 48, 49]	
BAS		56.7, 64, 68.5, 69	[26, 40]	
Et ₃ PO	Sn-BEA	Silanol groups	45.7	
		Free and/or physisorbed	39, 40.3, 48	
	MCM-41	LAS	54.9, 58.6	[50]
<i>n</i> -Bu ₃ PO	REH-Y ^a (RE = La, Ce)	BAS	56.7, 63.6, 75.9	[40]
		Free and/or physisorbed	47.2, 48	
		LAS	76	[41]
H-MFI	MCM-41	Free and/or physisorbed	50	
		BAS	71–92	[26, 49]
		Free and/or physisorbed	46–56	
<i>n</i> -Oct ₃ PO	MCM-41	BAS	56.6, 70, 73.7, 74	[26, 40]
		Free and/or physisorbed	47, 58	
		BAS	56.2, 73.7	[40]
Ph ₃ PO	H-Y	Free and/or physisorbed	47, 47.5	
		BAS	30	[37]
	USY	Free and/or physisorbed	24, 28	
		BAS	30	
		Free and/or physisorbed	24, 28	

^a (REH-Y) Faujasite zeolite modified with lanthanum and cerium chlorides.

³¹P MAS NMR spectra of adsorbed trimethylphosphine oxide.

The difference in the strength of Brønsted acid sites in zeolites can be explained not only by their structural features, but also with a difference in the Si/Al ratios. Zhao et al. [26] studied the acidity of H-MFI zeolites with different Si/Al ratios by the ³¹P MAS NMR spectroscopy

of adsorbed trimethylphosphine oxide (Fig. 15). A decrease in the Si/Al ratio increased the total intensity of signals assigned to Me₃PO complexes with BAS. Therewith, an increase in the contribution of low signals was observed. The spectrum of the sample with Si/Al = 15 displayed predominantly the signal at 63 ppm, while the spectrum of the sample with Si/Al = 75, the signal

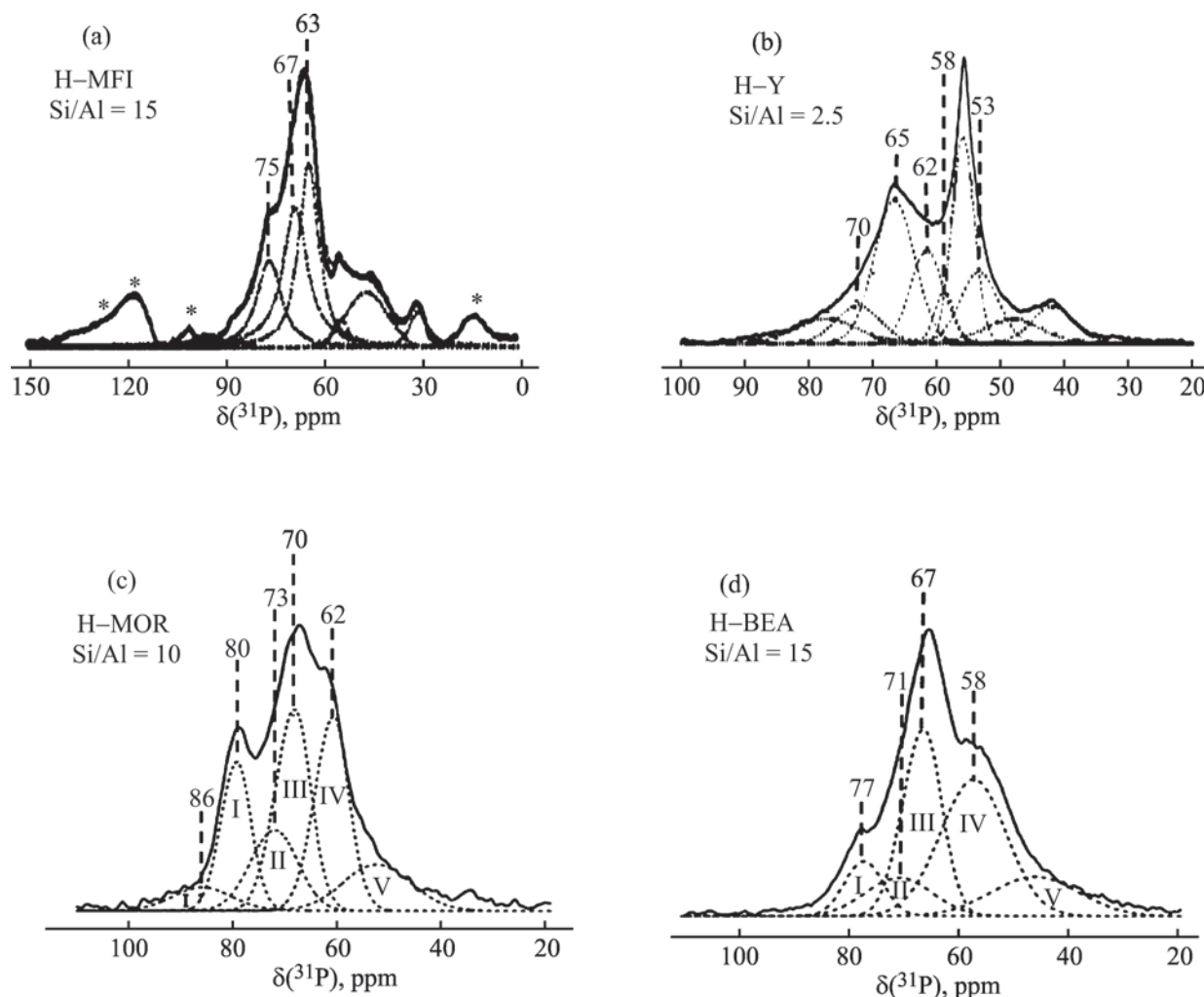


Fig. 13. ^{31}P MAS NMR spectra of trimethylphosphine oxide adsorbed on zeolites of different structural types: (a) MFI [26], (b) FAU [41], (c) MOR [22], and (d) BEA [22]. The dashed lines shows the signals assigned to Me_3PO adsorbed on BAS.

at 75 ppm. This finding suggests that an increase in the concentration of aluminium in the zeolite increases the total number of acid sites but decreases the strength of the latter.

2.2.2. Study of Lewis Acid Sites

The formation of Lewis acidity in molecular sieve materials can be accomplished in a number of ways. In Al-containing systems, LAS arise from dehydroxylation, dealumination, or other treatments leading to the formation of extralattice Al-containing fragments. In these systems, LAS always coexist with BAS. Another mechanism of LAS formation is associated with the isomorphic substitution of Si in the zeolite structure by other tetravalent elements. In this case, the material

possesses exclusively Lewis acidity and does not contain Brønsted sites. Such systems include materials like Sn-, Zr-, and Ti-containing molecular sieves, which have attracted great attention of researchers over the past years. The present section discusses the feasibility of the ^{31}P MAS NMR spectroscopy of adsorbed substituted phosphine oxides for characterization of LAS of different types.

Figure 16 compares the ^{31}P MAS NMR spectra of Me_3PO adsorbed on the H-Y zeolite, which contains BAS only (55 and 65 ppm), and an ultrastable USY zeolite, which contains both BAS and LAS. The signal at 37 ppm was assigned to Me_3PO adsorbed on LAS, but, as seen from the figure, this signal overlaps with the signals

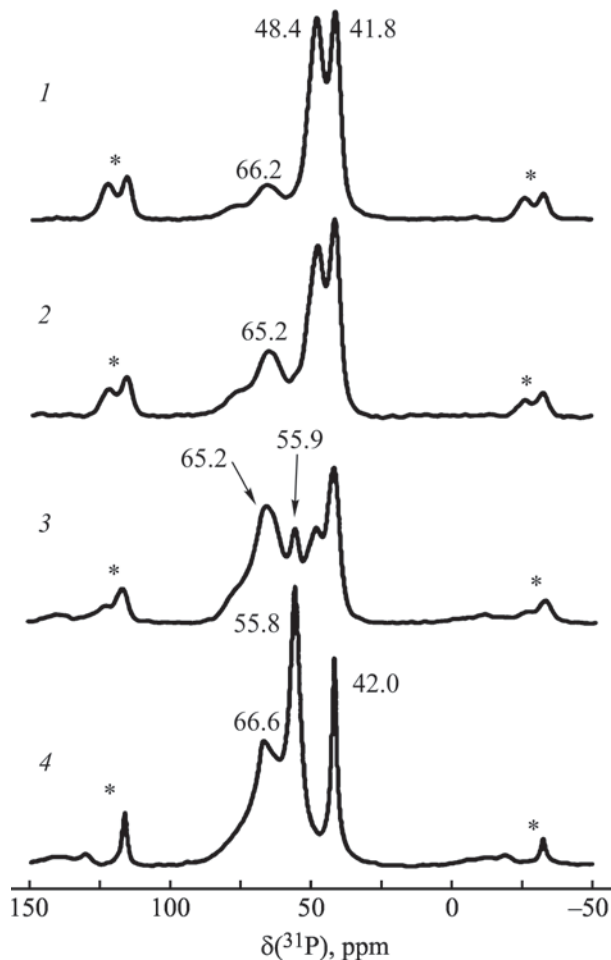


Fig. 14. ³¹P MAS NMR spectra of Me₃PO adsorbed on H,Na-Y zeolites with different degrees of Na⁺/H⁺ exchange: single ion exchange with (1) 0.01 M, (2) 0.02 M, and (3) 0.03 M and double ion exchange with (4) 1 M aqueous NH₄NO₃ followed by calcination [45].

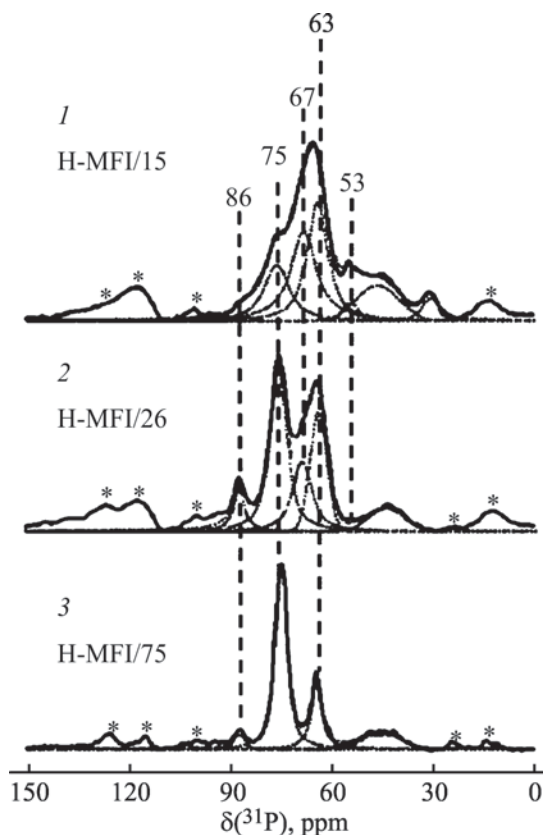


Fig. 15. ³¹P MAS NMR spectra of Me₃PO adsorbed on H-MFI zeolites with different Si/Al ratios. Si/Al ratio: (1) 15, (2) 26, and (3) 75 [26].

of free (39 ppm) and physisorbed Me₃PO (44 ppm), which makes the spectrum difficult to interpret [35].

Another example is provided by the study of Zhao et al. [42] on dealuminated H-BEA zeolites with different Si/Al ratios. To assign the signals in the ³¹P MAS NMR spectra to Me₃PO adsorbed on Brønsted or Lewis acid sites, the authors made use of selective poisoning of BAS with 2,6-dimethylquinolines (Fig. 17). As a result, the signals at 55–64, 67–71, and 81–85 ppm were assigned to Me₃PO adsorbed on BAS, and the signals at 49–50 and 65–66 ppm, to Me₃PO adsorbed on LAS. These findings suggest that the concentration of Lewis acid sites increases with increasing degree of dealumination.

Analysis of the reported data shows that studying LAS in Al-containing molecular sieves is complicated

by the fact that these systems also contain BAS. The signals of phosphine oxides adsorbed on LAS overlap with the signals of the probes adsorbed on BAS, as well as physisorbed probes, and it seriously complicates spectral assignment.

A different picture was observed in the case of systems with isomorphous substitution. Here substituted phosphine oxides can be considered as more promising probe molecules for characterization of LAS, because the corresponding spectral signals do not overlap with those associated with BAS.

Lewis et al. [50] studied the acidity of BEA zeolites with different heteroatoms (Sn, Hf, Zr, and Ti) by ³¹P MAS NMR spectroscopy of adsorbed Me₃PO (Fig. 18). Most data were obtained for Sn-BEA zeolite. Analysis of

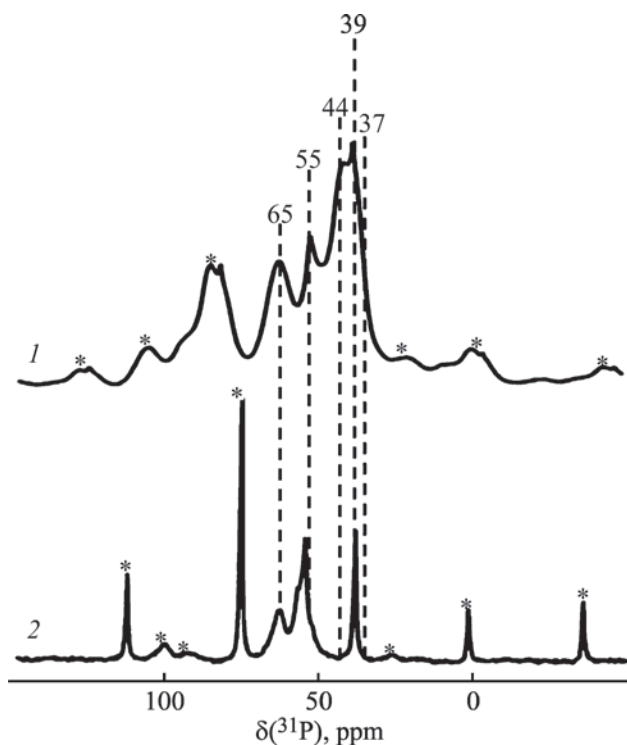


Fig. 16. ^{31}P MAS NMR spectrum of trimethylphosphine oxide adsorbed on (1) an ultrastable USY zeolite and (2) the starting H-Y zeolite [35].

the ^{31}P , ^{19}F , and ^{119}Sn MAS NMR spectra allowed the cited authors to identify 2 type of LAS and assign 2 signals (54.9 and 58.6 ppm), observed at low occupancies, to the complexes of these sites with one Me_3PO molecule, as well as 2 additional signals (57.2 and 59.9 ppm), that appear at high occupancies, to the complexes with two Me_3PO molecules (Fig. 18d). The assignment of signals in the ^{31}P MAS NMR spectra made it possible to correlate the concentrations of different types of LAS with the catalytic activity of zeolites in the isomerization of glucose and the aldol condensation of benzaldehyde and to evaluate the reactivity of different LAS in these reactions.

Similar results were obtained for zeolites with other heteroatoms (Hf, Zr, and Ti). The authors observed at least two signals in the range 50–60 ppm, corresponding to different LAS (Figs. 18a–18c). The chemical shifts of these signals were found to be strongly dependent on the electronic properties of the heteroatom, which acted as a Lewis acid site, and correlate with the reactivity of the zeolites.

Thus, it can be concluded that the ^{31}P MAS NMR spectroscopy of adsorbed phosphine oxides is quite a suitable tool to study BAS of different structures and strengths in Al-containing molecular sieves, as well as LAS in zeolites containing heteroatoms, such as Zr, Ti, and Sn. This method is of little use for characterizing LAS in Al-containing zeolites because of the strong overlap of the signals of trimethylphosphine oxides in complexes with BAS and LAS.

2.3. Determination of the Localization and Accessibility of Acid Sites

Like phosphines, substituted phosphine oxides with different sizes of the substituents can be used as molecular probes to evaluate the accessibility of acid sites in the porous structure of molecular sieves. The molecular size of Me_3PO is 0.55 nm [40]. Therefore, these molecules can readily penetrate into the porous system of medium- and wide-pore zeolites. Tri-*n*-butylphosphine oxide (molecular size 0.82 nm [40]) can reach only acid sites in wide-pore zeolites. The latter molecules can be used to study acidity on the external surface of crystalline narrow-pore and medium-pore zeolites. Triphenylphosphine oxide (molecular size 1.1 nm [37]) is used to study the acid sites on the external surface of crystalline wide-pore zeolites, as well as in mesoporous and hierarchical molecular sieves.

The discussed approach to the localization of acid sites was used in a number of works. The authors of [26, 41, 49] used *n*- Bu_3PO and Me_3PO as probes for assessing the accessibility of acid sites in a faujasite-type zeolite modified with lanthanum and cerium chlorides, as well as in H-MFI zeolite. Zhao et al. [26] made use of trimethyl- and tri-*n*-butylphosphine oxides and found that the concentration of Al in MFI zeolite does not affect the number of acid sites of the external surface of crystals but determines the number of acid sites inside pores.

Lakiss et al. [37] used trimethyl- and triphenylphosphine oxides as probes to evaluate the total acid sites and the acidity of the external surface of H-Y zeolite and an ultrastable Y (USY) zeolite. The signals in the ^{31}P MAS NMR spectra of adsorbed Ph_3PO were assigned to external surface acid sites, and the total amount of acid sites was evaluated using adsorbed Me_3PO . Comparing the results obtained with Me_3PO and Ph_3PO , the authors concluded that the fraction of acid sites located on the external surface of crystals in the USY zeolite is higher than in H-Y. The MAS NMR spectral data for adsorbed

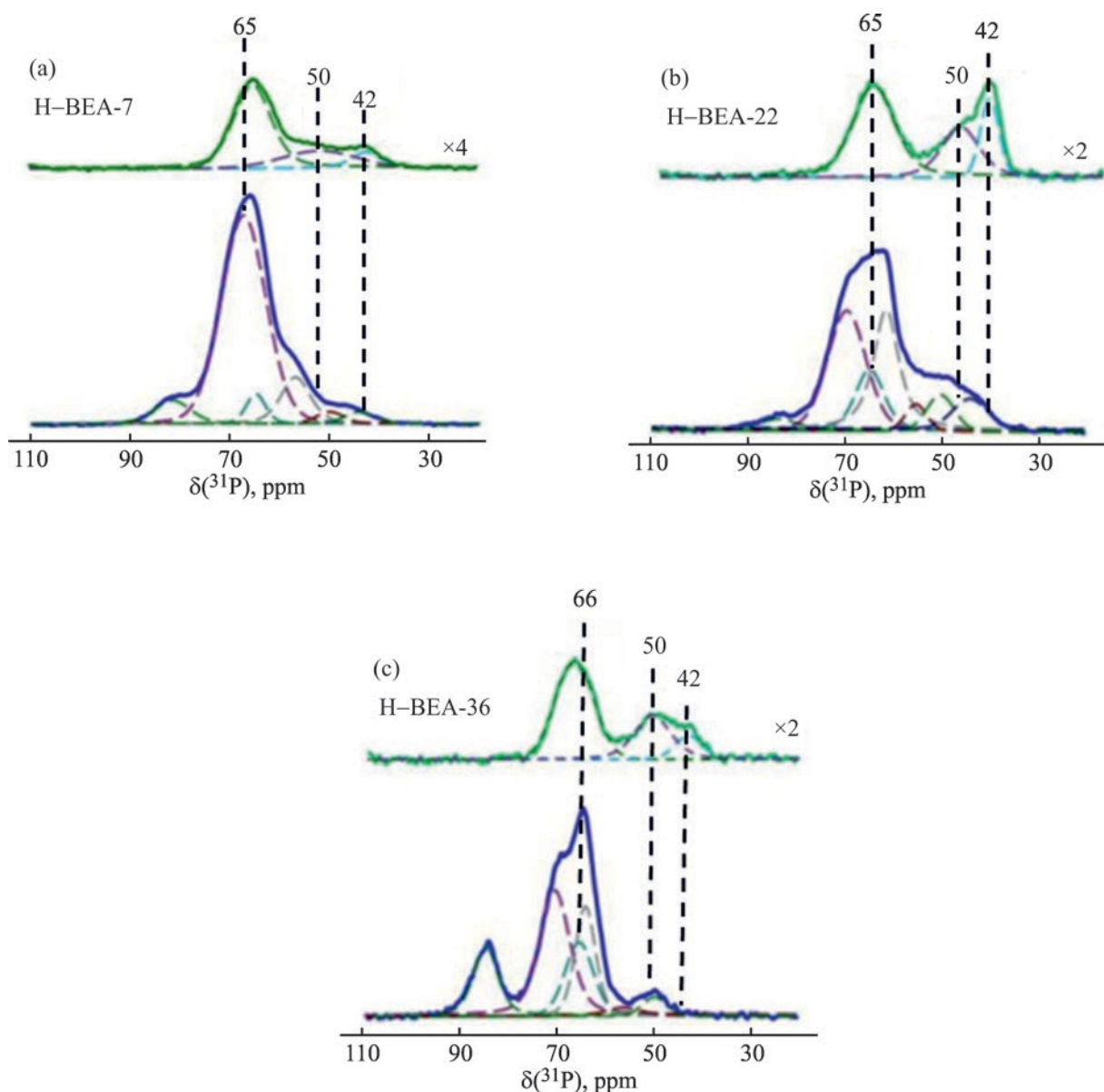


Fig. 17. ^{31}P MAS NMR spectra of trimethylphosphine oxide adsorbed on H-BEA zeolites with different Si/Al ratios, measured (lower spectrum) before and (upper spectrum) treatment [42]. Si/Al ratio: (a) 7, (b) 22, and (c) 36.

Ph_3PO are in good agreement with the IR spectral data for adsorbed tri-*tert*-butylpyridine.

2.4. Quantitative Determination of Acid Sites

The main approaches for the quantification of acid sites in the case of phosphine oxides do not differ from those for phosphines. Here, too, 2 approaches based on normalizing the intensity of the spectral signal to the total amount of phosphorus adsorbed on the sample and using an external standard. In the first case, the total amount of

phosphorus is often determined by inductively coupled plasma mass spectroscopy [35, 41, 46]. In the second case, diammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ is used as an external standard [19, 22].

With phosphine oxides, the errors in the estimation of the amount of acid sites arise from different reasons than with phosphines. Organophosphorus oxides are not prone to oxidation but are very hygroscopic. Therewith, according to [35], the chemical shifts and the intensity distribution along the lateral spinning sidebands of the

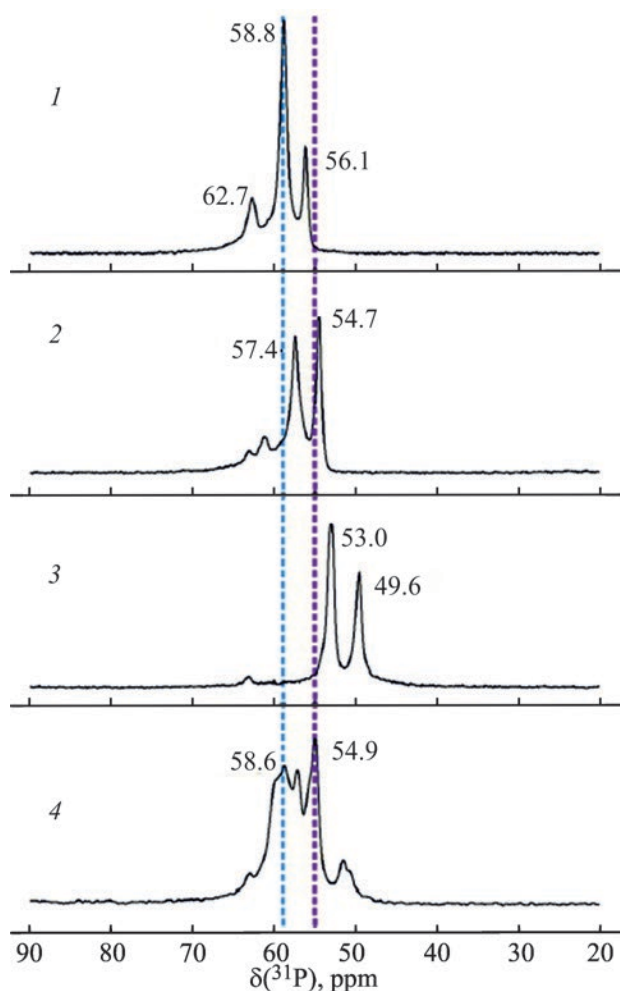


Fig. 18. ^{31}P MAS NMR spectra of trimethylphosphine oxide adsorbed on (1) Hf-BEA, (2) Zr-BEA, (3) Ti-BEA, and (4) Sn-BEA zeolites [50].

signals of pure, crystalline, and watered phosphine oxides strongly differ from each other. In this connection, these compounds should be manipulated under stringent moisture protection.

On the other hand, phosphine oxides are solids at room temperature. According to the sample pretreatment procedure, most frequently referred to in the literature and described in [44], before adsorption they should be dissolved in volatile solvents and applied to the samples by incipient wetness impregnation. This inevitably leads to other errors associated with both the purity of the reagents used and the application procedure itself.

CONCLUSIONS

Analysis of the literature allows us to conclude that the ^{31}P MAS NMR spectroscopy of adsorbed probes

holds great promise for research into the acid properties of molecular sieve catalysts. At present, a great body of evidence has been accumulated on the use of trisubstituted phosphines and their oxides for assessing the acidity of zeolites and zeolite-like materials of different structural types, assignment of spectral signals to acid sites of different nature, and methodological approaches to the determination of the number, strength, and localization of acid sites of different types.

It was found that trisubstituted phosphines can be used as effective probe molecules for determining the concentration of Brønsted acid sites. The signals of protonated substituted phosphines in the ^{31}P MAS NMR spectra do not overlap with the signals of these molecules both physisorbed and adsorbed on Lewis acid sites. However, substituted phosphine probes are impossible to use to evaluate the strength of BAS, because their signals appear in a very narrow spectral range. On the contrary, when it comes to Lewis acid sites, phosphines are suitable probes for evaluating the strength of these sites but do not provide reliable information on their number, which is explained by the fact that the spectral range of phosphines interacting with LAS overlaps the range of physisorbed molecules. Another disadvantage of substituted phosphines is their tendency for oxidation during sample preparation.

Trisubstituted phosphine oxides as probes offer some advantages over phosphines, in particular due to their oxidative stability. The main advantage of organophosphorus oxides consists in their sensitivity to the nature and strength of Brønsted acid sites. This allows one to differentiate between BAS of different types and to obtain more detailed information on their strength. Furthermore, the use of trisubstituted phosphine oxides holds great promise for studying LAS in zeolites containing such heteroatoms as Zr, Ti, and Sn. However, this method is unsuitable for the characterization of LAS in Al containing zeolites because of the signals of phosphine oxide probes adsorbed on BAS and LAS strongly overlap with each other.

Varying the size of the substituents in phosphine and phosphine oxide molecules makes it possible to determine the localization of acid sites and their accessibility for substrates of different sizes. Methyl-substituted phosphines and phosphine oxides readily penetrate into the porous system of zeolites and zeolite-like materials, which allows evaluation of the total acid site number. Using phosphines and phosphine oxides with bulkier

substituents (*n*-butyl-, *n*-octyl, and phenyl) allows evaluation of the amount of acid sites on the external surface of zeolite crystals and in mesopores.

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FUNDING

The review was funded by the Russian Science Foundation (project no. 19-73-10160).

CONFLICT OF INTEREST

I.I. Ivanova is the Chief Editor of the journal “Advanced Molecular Sieves.” The other authors declare no conflict of interest requiring disclosure in this article.

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