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Solid-state ^{51}V NMR and its potentiality in investigation of vanadia systems with paramagnetic centres

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ABSTRACT

In this article we will discuss the potentiality of solid-state ^{51}V NMR technique to characterize heterogeneous catalysts containing paramagnetic cations located on the surface or incorporated in the bulk of heterogeneous catalysts. ^{51}V NMR data for a number of 3d and rare earth vanadates, where paramagnetic effects are caused by the presence of paramagnetic cations, are considered. We also summarize results available for vanadium bronzes, where some vanadium is in a paramagnetic V^{4+} state, and for some vanadium compounds, where closely spaced paramagnetic centers form diamagnetic pairs. The comprehensive ^{51}V chemical shift scale (database) for paramagnetic solids was compiled.

1. Introduction

Heterogeneous vanadia-based catalysis has been a traditional object for ^{51}V NMR spectroscopy starting with its earliest applications in late 1950s, after the discovery of the magnetic resonance phenomenon. A considerable number of research papers on this subject has been published, many using solid-state ^{51}V NMR as their primary research tool. We have reviewed the subject of ^{51}V NMR in catalysis on several occasions [1–4]. In this article we discuss possible applications of ^{51}V NMR technique in the investigation of catalysts and model compounds containing paramagnetic centers. The major attention is paid to the isotropic chemical shift and the value of chemical shit anisotropy as the parameters which often may be relatively easy obtained from nowadays routine one-pulse and spin-echo solid-state NMR experiments. ^{51}V chemical shift scale for different paramagnetic systems will be compiled using original and published ^{51}V isotropic chemical shifts data. It should facilitate retrieving important chemical information about complex heterogeneous catalytic systems.

In general, the effects of paramagnetic metal ions on NMR spectra (chemical shifts, relaxation times, etc.) are well described for paramagnetic molecules and paramagnetic solids with low and intermediate concentration of paramagnetic centers [5–7]. Paramagnetic shifts are particularly useful in discovering medium- and long-range structural information. Formally, the majority of paramagnetic effects may be incorporated into the effective second-rank hyperfine interaction (HFI) tensor, which can be directly probed by magnetic resonance experiments. The Fermi-contact and pseudo-contact contributions to the chemical shift are the most important in the context of the following discussion.

The Fermi-contact shift is associated with the isotropic contribution to the HFI tensor from the electron spin density located directly at the nucleus site. For paramagnetic ions of 3d elements unpaired electrons are not completely concentrated at the ion location, but are also transferred via direct delocalization and spin polarization to remote atoms. The pattern of electron spin delocalization is not easily predictable from first principles, especially for solids. This is one of the reasons why the information obtained from contact shift values is often limited to the general picture of the electron spin delocalization over the nearest nuclei active in NMR. In disordered paramagnetic systems with magnetically anisotropic paramagnetic centers there is an additional orientationally averaged contribution to the isotropic value of the chemical shift called the pseudo-contact, or dipolar shift. It originates from the anisotropy of the net electron spin moment connected with a susceptibility tensor fixed at the molecular structure. The most common representation for a pseudo-contact shift is given by [8] (see also Eqs. (35)–(40) from [7] for other equivalent forms of the equation for pseudo-contact shifts)

$$\delta_{pc} = \frac{1}{12\pi r^3}\left[\Delta\chi_{ax}(3\cos^2\theta - 1) + \frac{3}{2}\Delta\chi_{rh}\sin^2\theta\cos 2\varphi\right]$$

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with

$$\Delta\chi_{ax} = \chi_{zz} - \frac{\chi_{xx} + \chi_{yy}}{2}, \quad \chi_{rh} = \chi_{xx} - \chi_{yy}$$

where $\Delta\chi_{ax}$ and $\Delta\chi_{rh}$ are the axial and rhombic anisotropy parameters of the magnetic susceptibility tensor χ of a paramagnetic metal, while two angles θ and ϕ define the orientation of an electron–nucleus vector in the frame of the magnetic susceptibility tensor. Interpretation of the pseudo-contact shifts depends to a lesser extent on the electronic structure theory of molecules or solids, comparing with similar interpretations of the Fermi-contact shifts. Nevertheless, such interpretation often requires comparison to a diamagnetic analogue with similar geometry and charge distribution [8,9]. Note, that this simplified picture of electron–nuclear interactions is applicable only to the systems whose hyperfine shifts obey a Curie–Weiss Law and significant interaction between paramagnetic species at the experimental temperatures is absent. In more complex situations other approaches and methods, need to be applied [10–14].

While V^{5+} containing phases are directly characterized by conventional ^{51}V NMR, this is not the case for materials with vanadium atoms in lower oxidation paramagnetic states. It is possible, however, though indirectly, to obtain information concerning the nature, location and the oxidation state of vanadium centers from NMR spectra of neighboring atoms. An example of such an investigation for vanadium–phosphorus systems was reported by Li et al. [15] and later by Tuel et al. [16]. They have applied a so-called ^{31}P spin-echo mapping technique to probe vanadium paramagnetic centers by observing the ^{31}P chemical shift over a very large spectral region. In compounds containing only diamagnetic V^{5+} centers the ^{31}P NMR chemical shifts are in the range 20–40 ppm; at the same time for compounds containing paramagnetic V^{4+} and V^{3+} the ^{31}P NMR chemical shifts range from 1600 to 2600 ppm and at around 4650 ppm, respectively. The ^{31}P NMR line shift is directly proportional to the density of unpaired electrons. Thus, the ^{31}P NMR chemical shift has provided information about the number of paramagnetic vanadium species in the first coordination sphere of phosphorus atoms, as well as on the oxidation state of such species. Applying the spin-echo mapping technique to ^{51}V under ultrahigh-speed MAS (and large spectral width) conditions, it is possible to detect ^{51}V NMR signals of V^{5+} atoms in close proximity to paramagnetic centers.

2. Experimental part

^{51}V NMR measurements were performed on a Bruker AVANCE-400 spectrometer (105.2 MHz operational frequency for ^{51}V resonance) using spin-echo and one-pulse sequences for wide line and MAS techniques. MAS spectra of powders were recorded at the rotation frequencies up to 35 kHz using 2.5 mm (outer diameter) rotor and Bruker MAS NMR probe. Short 0.7 μs (16°) excitation pulses were used in one-pulse experiments. Delay between pulses varied in the range 0.1–3 s. Standard solid-state spin-echo pulse sequence with $\tau_1 \sim 100$ μs, $P_1 \sim 90^\circ$, and $P_2 \sim 30^\circ$ was used in some cases to record the precise line shape. All chemical shifts are referred to $VOCl_3$ as an external standard. Simulations of ^{51}V static and MAS NMR spectra were performed taking into account second-order quadrupole correction using general purposes simulation program NMR1 described earlier [17].

Synthesis of 3d and rare earth orthovanadates was performed as described in Ch. 2 of [18]. Monocrystals of vanadium oxides bronzes were synthesized according to [19]. Vanadium sulfide clusters $V_2S_4(S_2CR)_4$ (R = EtO, *i*-PrO, *n*-Bu_2N) were prepared as described in [20]. Sodium-doped binary vanadia–titania catalysts of n-Na_2O:20V_2O_5:(80 − n) TiO_2 composition (where n = 0–15 wt.%) were prepared by mixing aqueous solutions of vanadyl oxalate and sodium hydroxide with suspensions of titanium dioxide (anatase) followed by spray-drying and calcination as described elsewhere [21]. The assignment of the phases formed in the course of the preparation and the purity of individual compounds was checked using powder XRD. Details of pretreatment procedure are described in [22].

3. Results and discussions

3.1. Presence of paramagnetic cations

Early studies of the effects of the paramagnetic centers on the ^{51}V NMR spectra were usually performed with CW NMR spectroscopy. The most important results of ^{51}V CW NMR in vanadium oxides, bronzes, and various vanadates of s-, d- and f-elements have been summarized by Pletnev et al. [23], together with some experimental spectra, and several examples of the cluster MO-calculations of the electric field gradients and the magnetic interactions. Note, that from the practical point of view ^{51}V CW NMR spectroscopy used in these studies of vanadium compounds has certain advantages over modern Fourier-transform NMR spectroscopy. The most important is a possibility of recording extremely broad spectra with almost unlimited spectral width. At the same time, modern pulsed NMR experiments with the same samples would require extremely broad sweep widths, short high-power RF pulses and very high spinning speeds if MAS is to be applied. On the other hand, these new NMR approaches bring increased spectral resolution and the ability to resolve non-equivalent vanadium sites, which is impossible by CW NMR. This is why nowadays ^{51}V NMR spectra of solids are usually measured on pulse NMR spectrometers using combination of MAS technique and especially adopted pulse sequences. Examples of typical ^{51}V MAS NMR spectra for several vanadates of rare earth and 3d elements are presented in Figs. 1 and 2 with the corresponding spectral parameters given in Table 1. The ^{51}V quadrupolar coupling constant found for iron orthovanadate $FeVO_4$ is rather small, while for rare earth orthovanadates the quadrupolar coupling constant exceeds those found in meta and orthovanadates of the Group I and Group II elements [23]. The asymmetry parameter of the quadrupolar tensor is zero for most of these compounds. It was reported earlier by Pletnev et al. [24,25] that the ^{51}V NMR isotropic chemical shifts for Cr, Fe, Co, and Ni orthovanadates are shifted to low field compared with that of the reference KVO_3 solution. Indeed this is the case for $FeVO_4$, where the isotropic chemical shift in the 35 kHz MAS spectrum is at 17,000 ppm, i.e. at much lower field to the reference sample. Because of the considerable distance of 3.4 Å between vanadium atoms and the paramagnetic centers, the direct contact interactions of ^{51}V nuclei with electrons located on the partially occupied 3d shells is unlikely. This strong effect on the isotropic chemical shift can be explained by transfer of electron density from the magnetic d-electrons via the atomic orbitals of non-magnetic ions, vanadium and oxygen.

The isotropic ^{51}V NMR chemical shifts in rare earth orthovanadates can be presented as:

$$\delta_{iso} = \delta_0 + \delta_p$$

where δ_0 is the diamagnetic chemical shift originating from the electronic structure of the filled orbitals, and δ_p is the paramagnetic shift which may be formally considered as a sum of three (or more) terms:

$$\delta_p = \delta_{fc} + \delta_{pc} + \delta_{\mathrm{BMS}}$$

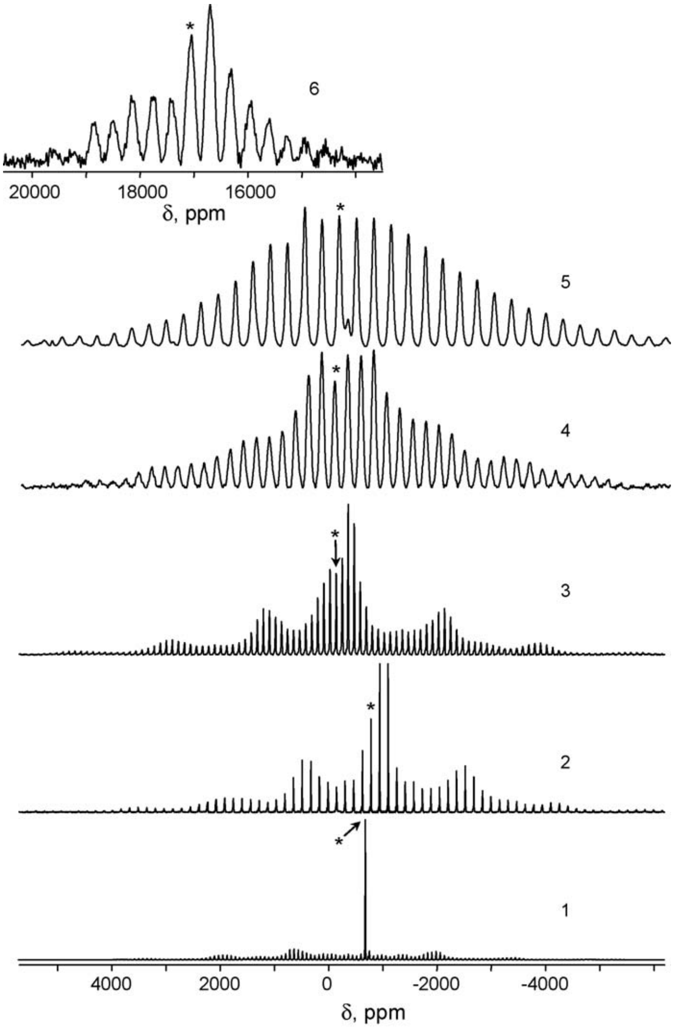

Fig. 1. The influence of M^{3+} cation on ^{51}V MAS NMR spectra of different rare earth orthovanadates: (1) $LuVO_4$ (diamagnetic compound); (2) $EuVO_4$ (paramagnetic due to the appreciable contribution of the excited state to the ground state of the Eu^{3+} ion); (3) $PrVO_4$; (4) $YbVO_4$; (5) $ErVO_4$; (6) $FeVO_4$ (3d paramagnetic orthovanadate with significantly larger contact contribution to the chemical shift).

Here δ_{fc} and δ_{pc} are the Fermi-contact and pseudo-contact terms due to the interaction of the vanadium atom with unpaired electrons of the M^{3+} ions, while δ_{BMS} is the isotropic part of bulk magnetic susceptibility (BMS) tensor [26–29].

For $\delta_{iso} = \delta_0$, as found in diamagnetic vanadates ($ScVO_4$, $LaVO_4$, $LuVO_4$ etc. [4]), the isotropic chemical shifts δ_{iso} are in the range typical for vanadium in an oxygen environment, i.e. $\delta_{iso} = \delta_0 \sim -600$ to -700 ppm. It is reasonable to assume that the δ_0 values are about the same for the whole range of the rare earth orthovanadates [30,31]. Therefore all the changes in δ_{iso} observed for rare earth vanadates are due to changes in δ_p. Also, there was no correlation found between the values of the isotropic chemical shifts and the *g*-factor anisotropy in ESR spectra [32,33]. Therefore, it may be proposed that contribution of the pseudo-contact interactions to the chemical shift is insignificant [30] and the differences in δ_{iso} for different orthovanadates in Table 1 have predominant contact nature. Moreover, the tendency of increasing δ_{iso} across the rare earth series clearly observed in Table 1 is consistent with earlier ^{51}V CW NMR results [30] obtained at low NMR frequencies.

It is seen from Fig. 1 that line width of the resonance increases in row $PrVO_4 < YbVO_4 < ErVO_4$. In this case line width is dominated by the anisotropic part of the dipolar interaction between electronic and nuclear spins, and correlates in general [34,35] with the magnetic moment of the rare earth cations. In fact, $g_J\sqrt{J(J+1)}$ is equal to 3.58, 4.54, and 9.58 for free trivalent lanthanides: $Pr^{3+}(^3H_4)$, $Yb^{3+}/^2F_{7/2}$ and $Er^{3+}(^4I_{15/2})$, respectively.

3.2. Systems with vanadium in mixed oxidation states. Vanadium bronzes and diamagnetic V^{4+}–O–V^{4+} (S=O) pairs

Vanadium bronzes are formed by incorporating M elements into the vacancies of the VO_n oxide structure. The charge balance is achieved by transferring two valence electrons of M ions to vanadium ions, which are nominally present in two oxidation states. To underline the fact that vanadium bronzes are actually oxides, sometime they are called oxide bronzes, or non-stoichiometric compounds incorporating one-, two-, and three-charged ions. Element M incorporated into the crystal structure of the oxide normally occupies only a fraction of the available voids, with the filling factor depending on the ionic radius of M^{n+}. By varying the concentration of M, it is possible to obtain a number of M_xVO_n phases with different composition [19]. Thus, depending on the *x* value, there are four such phases, α, β, γ, and δ for V_2O_5 [36]. One may expect that different types of phase transitions in $M_xV_2O_5$ obtained upon varying *x* could be followed with ^{51}V NMR. However, while studying $Li_xV_2O_5$ ($0.4 < x < 1.4$) Nakamura et al. [37] observed that for different values of *x* the isotropic ^{51}V chemical shifts did not change significantly. Based on this observation it was concluded that the VO_5 square pyramidal structure of V_2O_5 is retained without drastic structural modifications. However it is necessary to note that authors of [37] traced spectra changes only in the diapason characteristic for diamagnetic compounds for which the isotropic ^{51}V shift is not a very informative probe of the vanadium environment, the most informative being the value and the type of chemical shift anisotropy and the quadrupolar coupling constant [1–4]. According to this

Table 1
^{51}V NMR parameters for several vanadates of rare earth and 3d elements.

Compound	${}^{a}C_Q$ (MHz)	${}^{a}\eta_Q$	${}^{b}\delta_{iso}$ (ppm)	${}^{b}\delta_{\sigma}$ (ppm)	Electron configuration	$^{2S+1}L_J$ (atomic state)
$FeVO_4$	1.7	–	17,000	–	$3d^5$	$^{11}S_{5/2}$ (11)
$CeVO_4$	3.5	0.9	−559	200	$4f^1$	$^2F_{5/2}$ (6)
$PrVO_4$	5.59	0	−253	−520	$4f^2$	$^3H_4$ (9)
$NdVO_4$	5.5	0	−242	−550	$4f^3$	$^4I_{9/2}$ (10)
$EuVO_4$	4.95	0	−935	–	$4f^6$	$^7F_0$ (1)
$HoVO_4$	4.55	0	0	–	$4f^{10}$	$^5I_8$ (17)
$ErVO_4$	4.51	0	30	–	$4f^{11}$	$^4I_{15/2}$ (16)
$TmVO_4$	4.43	0	90	–	$4f^{12}$	$^3H_6$ (13)
$YbVO_4$	4.25	0	100	–	$4f^{13}$	$^2F_{7/2}$ (8)

[a] Values of C_Q and η_Q are from [23], these values are in an agreement with later results presented in [30,31].

[b] Values of δ_{iso} and $\delta_{\sigma} = \delta_{ZZ} - \delta_{iso}$ are obtained in this work.

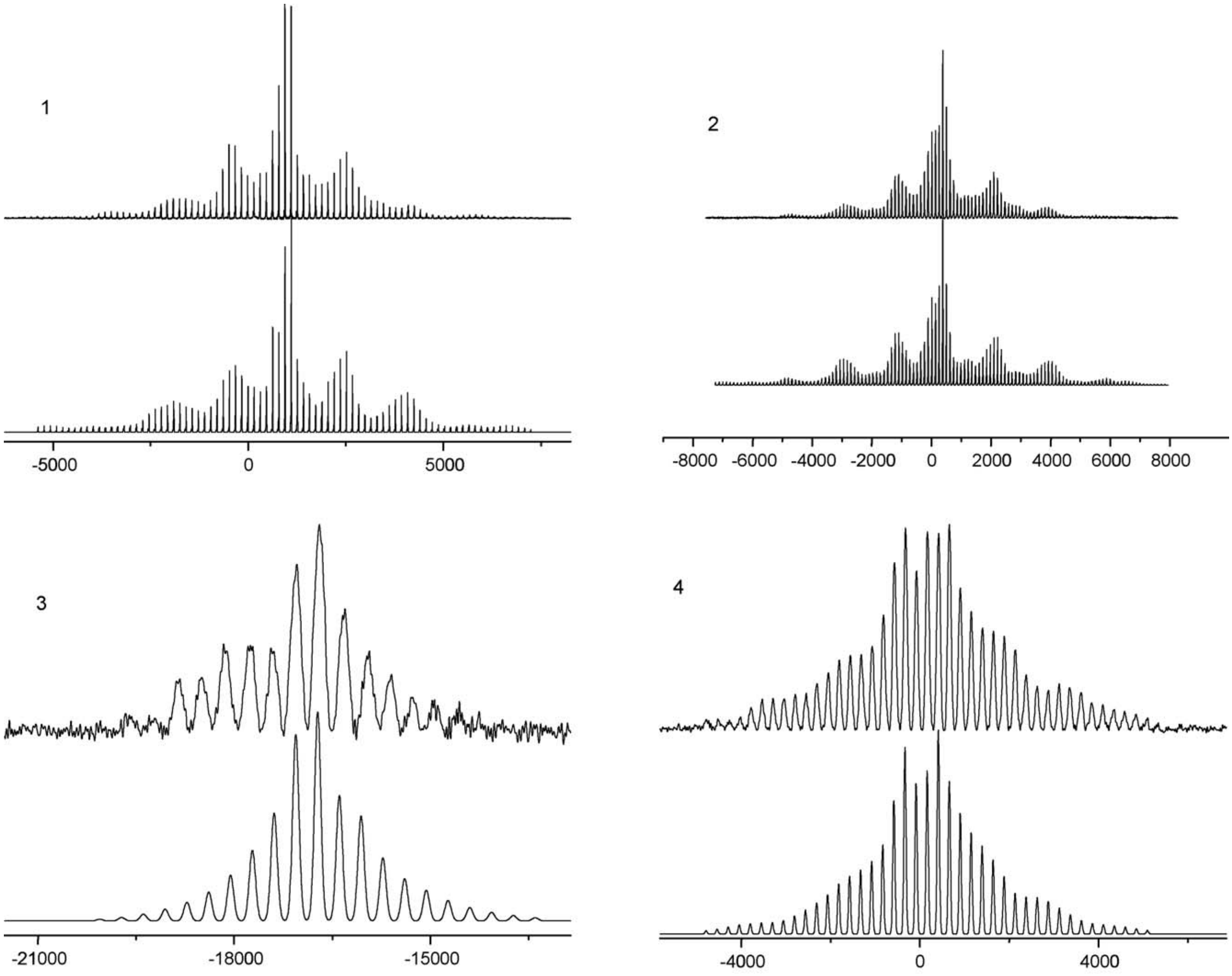

Fig. 2. Experimental (top) and simulated ^{51}V MAS NMR spectra of (1) $EuVO_4$; (2) $PrVO_4$; (3) $FeVO_4$; (4) $YbVO_4$.

comment and ^{51}V NMR spectra presented in [37] vanadium coordination is changed from square pyramidal structure of V_2O_5 to tetrahedral one with the variation of x.

The $\beta(\beta')$ type vanadium bronzes of Li, Na, K, Ag, Bi, and Sr are structurally similar (Table 2). The crystal structure of these bronzes can best be described as a strongly distorted V_2O_5 phase with three non-equivalent vanadium sites, V_1, V_2 and V_3. It is often assumed, although it is not certain, that the paramagnetic V^{4+} ions, or unpaired electrons, are located either in V_1 or V_2, or in both, while V^{5+} ions occupy only V_3. From the data presented in Table 2, it is clear that the line at −900 ppm is typical for all bronzes of the β type, and perhaps can be attributed to V^{5+} located near V^{4+}. If, however, V^{4+} ions or unpaired electrons occupy V_1 and V_2 sites, then V^{5+} shifted to the high field may also occupy V_1 and V_2 sites. In $Ca_{0.3}V_2O_5$ and $Cs_{0.35}V_2O_5$ bronzes ^{51}V NMR signals were detected at 2120 and 1565 ppm, respectively, which is very close to signals from diamagnetic V^{4+}–O–V^{4+} pairs in β-VO_2. This correlates with the non-magnetic state of $Ca_{0.3}V_2O_5$ at liquid He temperature. It is interesting, that in $Ca_{0.3}V_2O_5$ the ^{51}V NMR signal is at −4766 ppm, very close to metallic α-VO_2. In similar metallic bronzes ^{51}V NMR signals can be observed from −1718 to −739 ppm. The more metallic the bronze becomes, i.e. moving from $Na_{0.33}V_2O_5$ to $Na_{0.67}V_2O_5$, the more the ^{51}V NMR signal is shifted towards the signal found in pure vanadium metal (Table 2). Some representative ^{51}V NMR spectra for vanadium bronzes and VO_2 are shown in Fig. 3. It is important to recognize, that the interpretation of such spectra is not always straightforward, which sometimes leads to heated debates and controversy in the literature [38,39]. For example, the high-temperature phase of α-VO_2 is clearly metallic with characteristic anisotropy in properties, and at the same time this phase is characterized by the abnormal ^{51}V NMR chemical shift at −4788 ppm, and opposite in sign to the Knight shift in vanadium metal. This behavior can be explained by dominating contributions of the electron polarization transfer between ground electron orbitals and those with unpaired d-electrons. In a similar fashion, to describe the non-metallic diamagnetic electronic state of the low-temperature β-VO_2 phase, it was suggested to use either a model involving mixed oxidation states, V^{3+} and V^{5+}, or a model of the diamagnetic V^{4+}–O–V^{4+} (S=O) pairs. The latter model is more prevalent, and is supported by the isotropic ^{51}V NMR shift values found in four model compounds with Cuban-like structures containing diamagnetic pairs V^{4+}–S–V^{4+} (Fig. 3).

Combining the results above with the known from literature ^{51}V NMR chemical shift data for other paramagnetic compounds we compiled up to date the most comprehensive ^{51}V chemical shift scale which is presented in Fig. 4. These data may be useful for the interpretation of paramagnetic species/phases formed on the surface or in the bulk of vanadium containing heterogeneous catalysts.

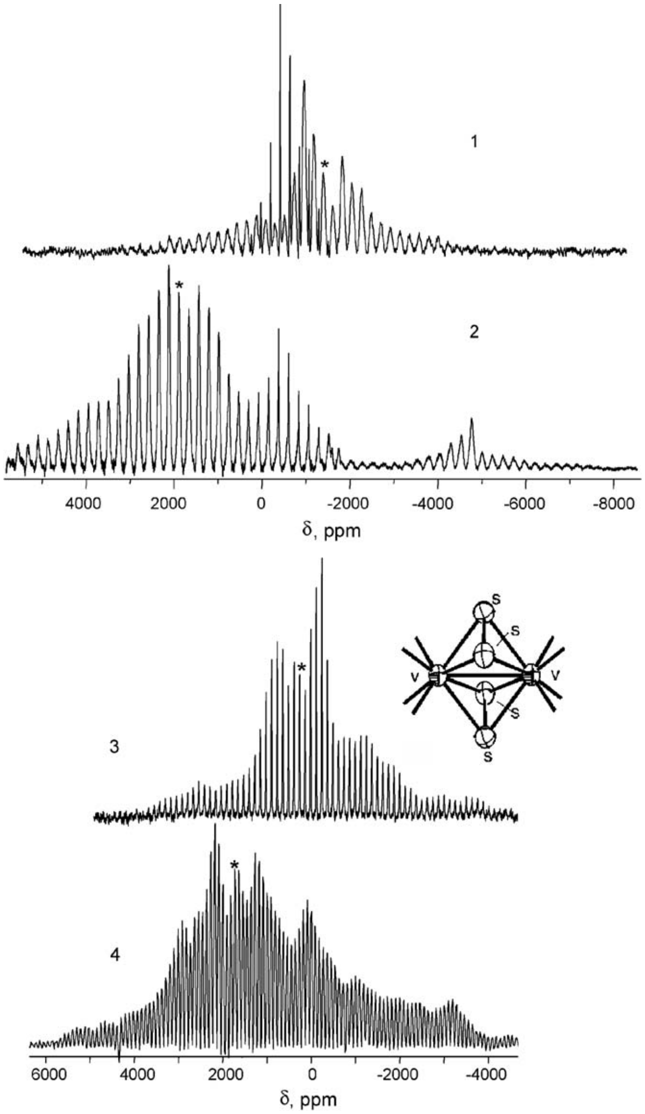

Fig. 3. 9.4T (30 kHz MAS) ^{51}V NMR MAS spectra of polycrystalline vanadium bronzes and two vanadium compounds with V^{4+}–V^{4+} pairs in the structure: (1) $Ba_{0.17}V_2O_5$; (2) $Ca_{0.3}V_2O_5$; (3) $V_2S_4(n\text{-}Bu_2NCS_2)_4$; (4) VO_2. Due to a very short distance between two V^{4+} ions these compounds are diamagnetic. Isotropic lines are marked with asterisks.

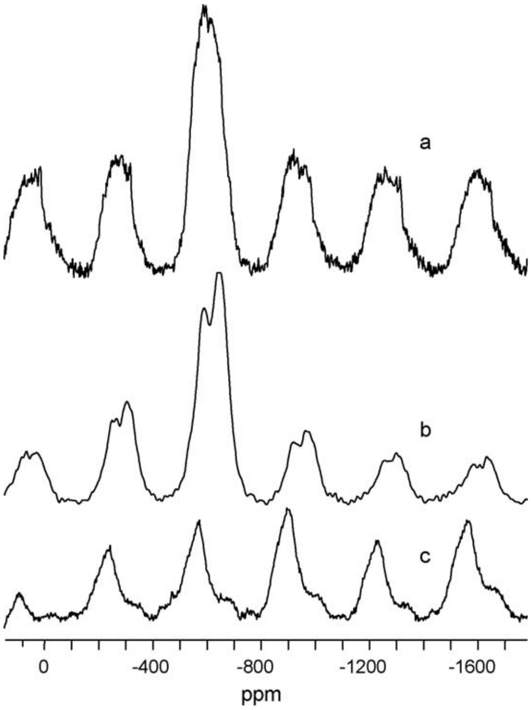

Fig. 5. ^{51}V NMR spectra of paramagnetic 3%Na–10%V/TiO_2 catalyst (a), diamagnetic VO_x/TiO_2 catalyst (b), and paramagnetic $Na_{0.33}V_2O_5$ bronze (c).

3.3. Vanadia-based catalyst

^{51}V NMR identification of the formation of $Na_xV_2O_5$ bronze may be illustrated on the example of paramagnetic sodium-doped binary vanadia–titania catalyst 3%Na–10%V/TiO_2 studied earlier by ^{23}Na and ^{51}V MAS NMR [22]. Using high speed (30 kHz) MAS technique and sensitive NMR probe it was possible to identify in this study both ^{51}V NMR signal typical for strongly bound vanadium species as well as the signal which may be attributed to the formation of $Na_xV_2O_5$ paramagnetic bronze (Fig. 5). The later signal was unassigned earlier because it was detected only implicitly as structureless broad ^{51}V NMR line. This example of solid-state ^{51}V NMR illustrates the advantages of high speed MAS technique for studying complex multi-component systems having practical importance. NMR approach has allowed to perform more detailed characterization of this catalyst.

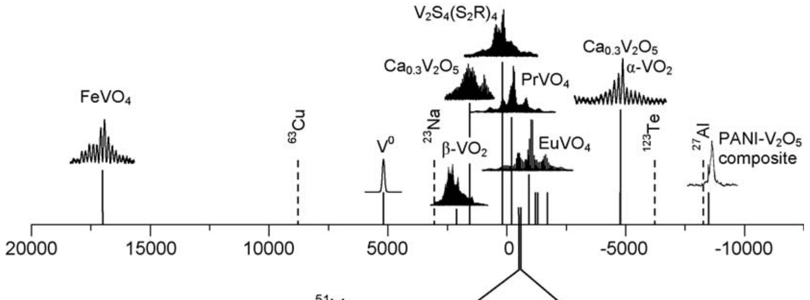

Fig. 4. ^{51}V NMR chemical shift scale for vanadium systems with paramagnetic centers. Solid vertical lines correspond to the isotropic shifts of the spectra presented in the figure, the dotted ones correspond to the resonance frequencies of the neighboring nuclei: ^{63}Cu, ^{123}Te, ^{23}Na, and ^{27}Al.

Table 2
Parameters of the ^{51}V NMR spectra in oxide bronzes and compounds containing V^{4+}–V^{4+}.

Compounds	C_Q (kHz)	η_Q	δ_σ (ppm)	η_σ	δ_{iso} (ppm)	Refs.
Cuban like compounds couples V^{4+}–S–V^{4+}, V^{4+}–O–V^{4+}						
$V_2S_4(S_2COEt)_4$	3120	0.4	−960	0.001	70	This work
					54	
$V_2S_4(S_2COi\text{-}Pr)_4$	3120	0.4	−960	0.001	105	This work
					82	
					56	
$V_2S_4(S_2CNBu_2)_4$	3126	0.40	−956	0.001	135.0	This work
4,4′-Bipyridinium cations, $(C_{10}H_{10}N_2)[(VO_2)_4(PO_4)_2]$					−580.1	[39]
					−593.4	
					−599.2	
Metal						
Metal V	–	–	–	–	5200	This work
Oxides						
β-VO_2	6940	0.46	1151	0.88	2113	[40]
α-VO_2	1.9	0.4	175		−4788	[40]
Bronzes						
$Ca_{0.3}V_2O_5$	2100	0.9	270	1.0	2120	This work
	4000	0.9	1000	–	−4766	
$Bi_4V_2O_{10.6}$					−1447	[41]
$Cs_{0.35}V_2O_5$			1000		1565	This work
			800		−775	
			800		−810	
$Na_{0.67}V_2O_5$	–	0.9	370	0.8	−739	This work
$Li_{0.3}V_2O_5$	–	–	835	0.92	−869	This work
$Na_{0.33}V_2O_5$	4000	–	1600	–	−1200	This work
					−900	
$K_{0.25}V_2O_5$					−620	This work
					−900	
$Ag_{0.35}V_2O_5$					−435	This work
					−900	
$Sr_{0.17}V_2O_5$	–	–	860	–	−1718	This work
$Ba_{0.17}V_2O_5$	–	–	1250	0.01	−1381	This work
Composites						
PANI-V_2O_5-nanocomposites					−8500	[42]

4. Conclusion

On the example of ^{51}V MAS NMR of paramagnetic materials and catalysts we have demonstrated the potentiality of this method as a practical tool of further investigations in heterogeneous catalysis and material science. Solid-state NMR provides a unique possibility for learning the structure and the underlying properties of these materials in great detail. The availability of advanced NMR hardware, including ultrahigh magnetic fields and ultrahigh-speed MAS probes will make ^{51}V NMR experiments on paramagnetic solids feasible and will further expand the borders of catalytic applications of ^{51}V NMR spectroscopy. We have compiled the comprehensive ^{51}V chemical shift scale (database) for paramagnetic solids and hope that this data will contribute to ever continuing progress in development of novel solid-state NMR techniques for catalytical applications.

Acknowledgements

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