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Effect of positional isomerism and vanadium substitution on ^{51}V magic angle spinning NMR Spectra Of Wells-Dawson polyoxotungstates

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ABSTRACT

We examined the positional isomerism and vanadium substitution on the ^{51}V magic angle spinning NMR spectra of potassium salts of vanadium-substituted polyoxotungstates of the Wells-Dawson series. NMR parameters of this class of catalytically active polyoxotungstates effect of are reported. Multiple species, indicative of differences in the local environment at the substitution sites, are observed in solid-state NMR spectra of the di- and tri- substituted complexes in contrast to solution NMR spectra, where single average chemical shift was observed. The quadrupolar and chemical shift anisotropy parameters depend strongly on the position and the degree of the vanadium substitution into the oxoanion core establishing ^{51}V SATRAS NMR spectroscopy as a sensitive probe of the local electronic environment in these catalytically active solids.

1. Introduction

Wells-Dawson phosphotungstates are known since 1892, when the synthesis of the first compound of the series was reported by Kehrmann [1]. The first crystal structure was reported by Dawson in 1953. Since the first discovery of the Wells-Dawson anion, these compounds have found a wealth of applications due to their versatile chemical and physical properties [2]. Wells-Dawson heteropolyoxometalates are utilized as heterogeneous and homogeneous catalysts in various types of processes, in solution and gas phase [2]. Vanadium-substituted polyoxoanionic compounds are used as catalysts in oxidation of NADH, aerobic oxidation of alkyl aromatic compounds, selective epoxidation of alkenes and alkenols with H_2O_2, benzene hydroxylation with H_2O_2, toluene and nitrobenzene oxidation with H_2O_2 (reviewed by Briand et al. [2]).

Vanadium derivatives of Wells-Dawson polyoxoanions are efficient in catalyzing the vapor-phase dehydrogenation of cyclohexanol [3], oxidation of tetralin by molecular oxygen [4], direct conversion of light C_1-C_3 alkanes into the corresponding carboxylic acids [5], and other transformations [6–10]. In all of the above cases vanadium substitution enhances dramatically the catalytic activity of the oxoanions, suggesting that vanadium modulates the electronic structure of the anion affecting the redox potentials. Vanadium-substituted polyoxometalates with enhanced activities for heterogeneous catalysis of hydrocarbon oxidation are generated as supported on mesoporous MCM-41 [11]. Due to these expanding applications of Wells-Dawson heteropolycompounds in catalysis, the interest toward development of novel representatives of this family continues to grow [12–15].

To gain insight on the structure-function relationships of the Wells-Dawson heteropolycompounds, understanding the mechanism by which vanadium fine-tunes the chemical reactivity of the catalyst is necessary. This understanding includes the knowledge of both the three-dimensional geometry of the extended solid (available from the single crystal X-ray diffraction in the cases where the solid can be crystallized) and the electronic structure of the anion and of vanadium center in particular. Advancements in theoretical quantum chemical methods have allowed for the investigations of Wells-Dawson (and generally polyoxometalate solids) [16–20], and these studies are expected to aid in the interpretation of the experimental structural and spectroscopic data. We and others have shown that ^{51}V solid-state NMR spectroscopy can be used as a sensitive reporter of the structural and electronic environment of vanadium sites in a wide variety of inorganic and bioinorganic solids [21–39] including polyoxometalates [40–42]. Specifically, in our previous MAS NMR studies on Lindqvist

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and Keggin polyoxotungstate solids, we have demonstrated that insights unavailable from X-ray diffraction and other structural methods could be gained, namely that counter cations and the degree of vanadium substitution modulate the electronic structure of the oxoanion as is evident in the ^{51}V magic angle spinning (MAS) NMR spectra [40,41] as well as vibrational spectra [16]. Since Wells-Dawson polyoxometalates have been utilized for homogeneous and heterogeneous catalysis, characterization of the electronic and structural properties of these complexes in both liquid and solid phase is needed to investigate their catalytic activities, dependence on metal ion substitution, and redox properties. This work establishes ^{51}V MAS NMR spectroscopy as a quick non-destructive structural probe in polyoxometalate solids that is especially useful in the absence of long-range order and for the investigation of electronic properties of these complexes as catalysts in solid phase.

In this study, we assess the utility of ^{51}V MAS NMR spectroscopy for structural analysis of vanadium-substituted heteropoly compounds of Wells-Dawson family. We present an investigation of four vanadium-substituted Wells-Dawson solids. In contrast to solution NMR spectroscopy, multiplet patterns were observed for di- and tri-substituted complexes, indicating that the different vanadium atoms are magnetically non-equivalent in the solid state. The results reveal that the ^{51}V NMR parameters in these polyoxotungstates depend on the degree and the position of vanadium substitution into the oxoanion thus indicating that ^{51}V MAS NMR spectroscopy is a sensitive probe of local environment of vanadium in the Wells-Dawson type of compounds.

2. Materials and methods

2.1. Materials and syntheses

All chemicals were obtained from Aldrich or Fisher and used without further purification: sodium tungstate dihydrate (Na_2WO_4•$2H_2O$) and sodium metavanadate ($NaVO_3$) were purchased from Aldrich Chemicals. Hydrochloric acid, phosphoric acid (85%), sulfuric acid, and bromine were purchased from Fisher Scientific.

1-$K_7P_2VW_{17}O_{62}$•$18H_2O$ (α_2-isomer) (I) was obtained with 10 g yield (40.6%) from 25 g α_2- $K_7P_2W_{17}O_{61}$•$20H_2O$ according to the published procedure [43].

4-$K_7P_2VW_{17}O_{62}$•$17H_2O$ (α_1-isomer) (II) was obtained with 8 g yield (30%) from 25 g α_1- $K_7LiP_2W_{17}O_{61}$•$20H_2O$ according to the published procedure [43].

1,2 - $K_8P_2V_2W_{16}O_{62}$ (III) was obtained with 4.6 g yield (10%) from 25 g α_2- $K_7P_2W_{17}O_{61}$•$20H_2O$ according to the published procedure [43].

1,2,3 - $K_9P_2V_3W_{15}O_{62}$ (IV) was obtained with 2.8 g yield (15%) from 25 g α_2- $K_7P_2W_{17}O_{61}$•$20H_2O$ according to the published procedure [43].

The schematic representations of the structures of the corresponding oxoanions are depicted in Fig. 1.

2.2. Solution NMR spectroscopy

^{51}V and ^{31}P solution NMR spectra were acquired at 9.4 T on a JEOL GSX-400 spectrometer equipped with Delta data system. The ^{51}V and ^{31}P resonance frequencies were 105.12 and 161.87 MHz, respectively. All spectra were acquired using a 5 mm broadband probe. ^{51}V spectra were acquired using a 5.8 μs (30°) single pulse; ^{31}P spectra were acquired with a 15 μs (90°) single pulse. 2048 complex FID points were collected. For ^{51}V, the total acquisition time of 48.7 ms, and the recycle delay of 500 ms were used. For ^{31}P, a recycle delay of 2 s was used. The ^{51}V and ^{31}P spectra were processed with 2 Hz exponential line broadening; no zero filling was applied. The isotropic chemical shifts are reported relative to the neat $VOCl_3$ sample and H_3PO_4 (85%), respectively, used as the external reference.

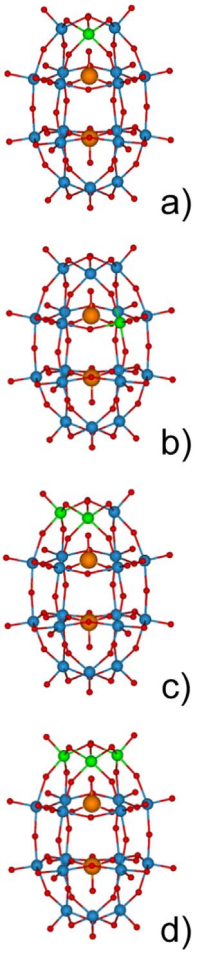

Fig. 1. The schematic representations of vanadium substituted polyoxotungstate anions: (a) 1-$K_7P_2VW_{17}O_{62}$•$18H_2O$ (α_2-isomer) (I); (b) 4-$K_7P_2VW_{17}O_{62}$•$17H_2O$ (α_1-isomer) (II); (c) 1,2 - $K_8P_2V_2W_{16}O_{62}$ (III); (d) 1,2,3 - $K_9P_2V_3W_{15}O_{62}$ (IV). The molecules are depicted in a ball-and-stick representation. In the anion, the tungsten atoms are shown in blue, the central P atoms are shown in orange, and the oxygen atoms are shown in red. The vanadium atoms are shown in green.

2.3. Solid-state NMR spectroscopy

Solid-state ^{51}V NMR spectra were acquired on a Tecmag Discovery spectrometer operating at 105.2 MHz (9.4 T). A 4 mm Doty XC4 MAS probe was employed. In general, 8–16 mg of samples were loaded into 4 mm Si_4N_3 rotors. For each compound, ^{51}V MAS NMR spectra were acquired at several spinning frequencies ranging from 4 to 17 kHz. The spinning frequencies were controlled to within ± 5 Hz. The vanadium chemical shifts were referenced with respect to neat $VOCl_3$. The 90° pulse-widths of 3.1 μs ($\gamma B_1/2\pi \approx 80$ kHz) were employed (calibrated using neat liquid $VOCl_3$). The magic angle was set by maximizing the number of rotational echoes observed in the ^{23}Na NMR free-induction decay of solid $NaNO_3$. All MAS spectra were acquired using a single-pulse excitation. 1 μs pulse was employed to excite the central and the satellite transitions. 1 s recycle delay was used. The spectral width was 1.25 MHz. A total of 4096 complex data points were acquired. The data were processed by linear prediction of the first points to suppress the baseline distortions, followed by Fourier transformation and baseline correction.

2.4. Simulations of the NMR spectra

Numerical simulations of the experimental ^{51}V solid-state NMR spectra were performed on a 1.1 GHz Pentium-4 PC under Linux environment using SIMPSON [44]. The combined effects of the

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