

Short communication

Characterization of V_2O_5 – $AlPO_4$ catalysts by ^{51}V and 1H magic-angle spinning solid-state nuclear magnetic resonance spectroscopy ^{*}

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Abstract

Amorphous aluminum orthophosphate is used as a carrier for preparing a series of V_2O_5 – $AlPO_4$ catalysts with varying vanadia content. The catalysts were characterized by solid-state ^{51}V and 1H magic-angle spinning nuclear magnetic resonance (MAS NMR), electron spin resonance (ESR) and X-ray diffraction (XRD). The XRD patterns of the catalysts remained amorphous at all loadings studied. ^{51}V Solid-state NMR spectra revealed the presence of V_2O_5 microcrystallites at higher vanadia loadings. The 1H MAS NMR spectra of the catalysts showed a maximum consumption of support hydroxyl groups at 6 wt.-% V_2O_5 indicating the completion of a monolayer at this composition.

Keywords: V_2O_5 – $AlPO_4$ catalysts; ^{51}V magic-angle spinning nuclear magnetic resonance; 1H magic-angle spinning nuclear magnetic resonance

1. Introduction

Supported vanadia catalysts are well known in catalyzing a great variety of reactions such as ammoxidation [1,2], selective oxidation [3,4] and NO_x reduction [5]. Spectroscopic techniques such as Laser Raman spectroscopy [6,7], X-ray photoelectron spectroscopy [8,9], ESR [10,11], extended X-ray absorption fine structure [12] and ^{51}V and

1H solid-state MAS NMR [13–15] have previously been employed in the structure elucidation of supported vanadia catalysts. The solid-state ^{51}V NMR spectroscopic studies of supported vanadia catalysts reported previously gave evidence for the presence of amorphous and crystalline vanadia species depending on the vanadia content in the catalyst samples. Recently, the development of MAS has afforded high-resolution NMR spectra of nuclei of interest in solid samples. Thus 1H , ^{13}C , ^{21}Al , ^{29}Si and ^{31}P MAS NMR spectroscopic studies have been employed for the structural analysis of zeolites, aluminas

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and aluminosilicates [16]. The ^1H MAS NMR studies allow for the quantitative estimation of hydroxyl groups on the support surface. A decrease in the OH group concentration upon active component loading indicates a strong metal oxide–support interaction.

In recent years, a number of papers [17–19] on support modification with additives such as phosphates, sulfates, alkali metal cations, halides, etc. have been reported. The modifiers were reported to have a positive effect on the dispersion of the active component and the activity of the catalysts. It has been shown recently that phosphate modification of $\gamma\text{-Al}_2\text{O}_3$ and SiO_2 improved the dispersion of V_2O_5 and the methanol partial oxidation activity of the catalysts [18,19]. The AlPO_4 -like species formed upon phosphate modification of the $\gamma\text{-Al}_2\text{O}_3$ support was thought to influence the dispersion of MoO_3 and consequently its hydrodesulfurisation (HDS) activity [20]. Amorphous aluminum orthophosphate itself has been used as a support for metallic catalysts [21]. However, there are not many reports on the use of amorphous AlPO_4 as a support for transition metal oxides as active ingredients. Recently, we have reported on the structure and activity of AlPO_4 -supported MoO_3 and WO_3 catalysts [22,23]. In this communication the results on the characterisation of $\text{V}_2\text{O}_5\text{-AlPO}_4$ catalysts by ^{51}V and ^1H solid-state NMR are presented.

2. Experimental

2.1. Preparation

Support

Aluminum phosphate was precipitated at a pH of about 8 by adding ammonia to an aqueous solution containing $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and the quantity of 85% H_3PO_4 (BDH chemicals), required to obtain a P/Al ratio of 1. The precipitate was oven-dried at 110°C for 16 h after thorough washing with distilled water and then calcined in air at 600°C for 5 h. The X-ray amorphous AlPO_4 thus obtained had a BET surface area of $63\text{ m}^2/\text{g}$.

Catalysts

A series of $\text{V}_2\text{O}_5\text{-AlPO}_4$ catalysts with vanadia content varying between 2 and 12 wt.-% were prepared by impregnating AlPO_4 with an aqueous solution containing a known amount of ammonium metavanadate. The dried catalysts were calcined in air at 500°C for 6 h.

X-Ray diffraction

XRD patterns of the catalysts were recorded on a Philips PW 1051 X-ray diffractometer with nickel-filtered $\text{CuK}\alpha$ radiation.

2.2. Solid-state NMR

The ^{51}V NMR spectra were recorded on an MSL-400 Bruker spectrometer at a 105.2-MHz frequency. The pulse duration was $1\ \mu\text{s}$ and the pulse repetition frequency was 10 Hz. The spectra were recorded with the use of polymethyl methacrylate rotors. The rotation frequency was 4–5 kHz. The chemical shifts were measured relative to VOCl_3 as an external reference.

The ^1H MAS NMR spectra were recorded at a frequency of 300.09 MHz. The frequency range was 50 kHz. The $(\pi/2)$ pulse duration was $5\ \mu\text{s}$ and the pulse repetition frequency was 1 Hz. Prior to NMR experiments the samples were placed in special NMR tubes, then evacuated at 250°C and 10^{-3} Pa for 24 h and sealed off. The spinning was performed in quartz rotors at a frequency of 3–3.5 kHz using a probe with minimal background signal. The probe head, rotor and the sample tubes were dried in order to remove the traces of water from their outside surface. The chemical shifts were measured relative to tetramethylsilane (TMS) as an external standard. The concentration of OH groups was determined by comparing the signal intensity of the catalyst with that of a known standard sample (SiO_2 evacuated at 300°C for 4 h contained $5 \cdot 10^{19}$ OH groups).

3. Results and discussion

The $\text{V}_2\text{O}_5\text{-AlPO}_4$ catalysts were found to be X-ray amorphous at all loadings studied. Since

XRD is a less sensitive technique, that can detect crystallites $> 40 \text{ \AA}$ only the possibility of the presence of V_2O_5 microcrystallites at higher loadings cannot be ruled out. Unlike XRD, which is a bulk technique, ^{51}V NMR and ^1H MAS NMR were found to be useful techniques for the differentiation between interacted and crystalline vanadia species in supported vanadia catalysts. The ^{51}V NMR spectra of selected $\text{V}_2\text{O}_5\text{-AlPO}_4$ catalysts are shown in Fig. 1. Fig. 1a shows the spectra under static conditions and Fig. 1b those with MAS. The MAS spectra are helpful for attributing the static ^{51}V spectra. In the spectra three different lines, with different chemical shifts, can be seen. At the low vanadia concentration of 4 wt.-%, line A ($\delta = -880 \text{ ppm}$), corresponding to a vanadium atom in a regular tetrahedral environment, can be observed. Line B

($\delta = -560 \text{ ppm}$) can be ascribed to tetrahedral vanadium atoms in a distorted environment of oxygen atoms formed due to the association of surface vanadia species, which is indicated by the large line width of signal B compared with that of A. At a low vanadia concentration (4 wt.-%) lines A and B are present in the spectra. An increasing vanadia content results in the decrease of the relative intensities of lines A and B and the appearance of line C, this line being most intense in the spectrum of the sample having 12 wt.-% V_2O_5 .

The use of MAS results in a better resolution of the lines allowing the measurement of isotropic chemical shift values, δ_{iso} . The isotropic line A has $\delta_{\text{iso}} = -880 \text{ ppm}$ while for line B $\delta_{\text{iso}} = -560 \text{ ppm}$. However, the δ_{iso} value for octahedrally coordinated vanadium can be calculated from the

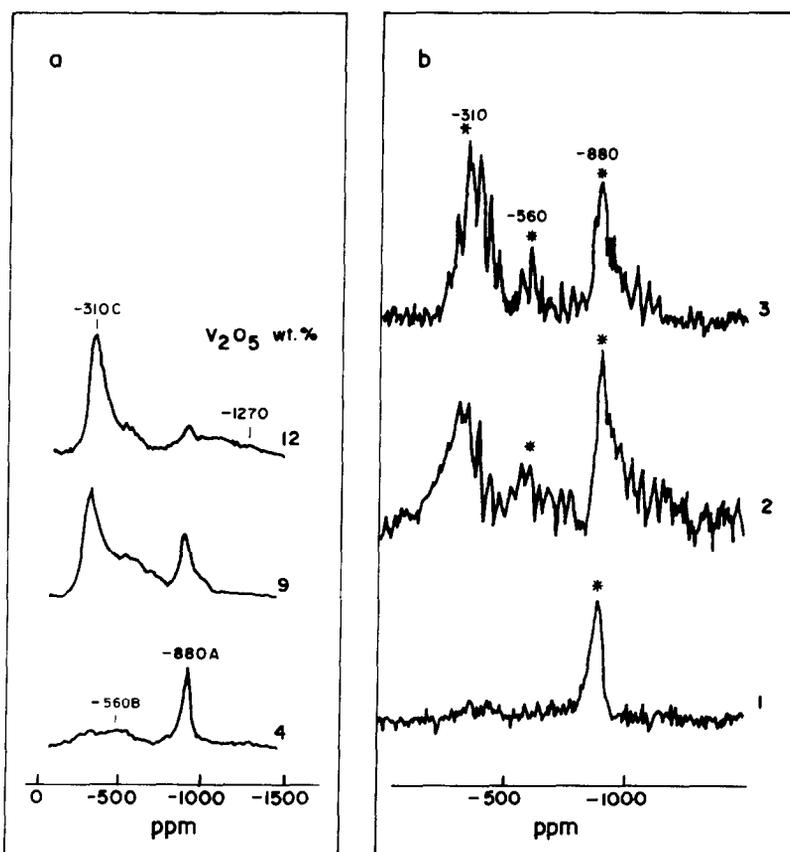


Fig. 1. (a) ^{51}V NMR static spectra and (b) ^{51}V NMR MAS spectra of $\text{V}_2\text{O}_5\text{-AlPO}_4$ catalysts.

static spectrum as $\frac{1}{3}(2\delta_{\perp} + \delta_{\parallel})$ which gives a value of -630 ppm. This value is typical of V_2O_5 [24]. On this basis line C can unambiguously be attributed to crystalline V_2O_5 formed on the $AlPO_4$ surface at the large vanadium concentration of 12 wt.-%.

Line A can be attributed to vanadia species in an almost regular tetrahedral environment, most probably with phosphorus atoms in their second coordination sphere as indicated by an unusually large δ_{iso} value. On the other hand, comparison of spectrum A with the δ_1 , δ_2 , δ_3 and δ_{iso} values for $VOPO_4$ and $VOPO_4-Al_2O_3$ compounds [24] revealed that this line cannot be ascribed to the formation of these compounds on an $AlPO_4$ surface. Line B, which has a δ_{iso} value typical of vanadium–oxygen tetrahedral complexes [24] and a larger linewidth than line A, can most probably

be attributed to the formation of tetrahedral vanadium clusters on the $AlPO_4$ surface. It may be noted that evacuation of the samples at $250^\circ C$ for 2 h does not influence the spectrum. This indicates that the surface vanadium species most probably do not contain hydroxyl groups or water molecules in their coordination sphere.

1H NMR spectra of pure $AlPO_4$ and $AlPO_4$ -supported V_2O_5 are shown in Fig. 2a. The spectrum of $AlPO_4$ expanded with computer simulation is shown in Fig. 2b. The spectrum of $AlPO_4$ resembles that of aluminum phosphate [25]. The spectra of $AlPO_4$ consist of several closely spaced overlapping lines from the P–OH group (peaks at $\delta = 6.4$ and 3.1 ppm). The line at $\delta = 0.5$ ppm can be attributed to the Al–OH group coordinated to one octahedral Al atom which is very close to that of the “basic” OH group in Al_2O_3 . The line

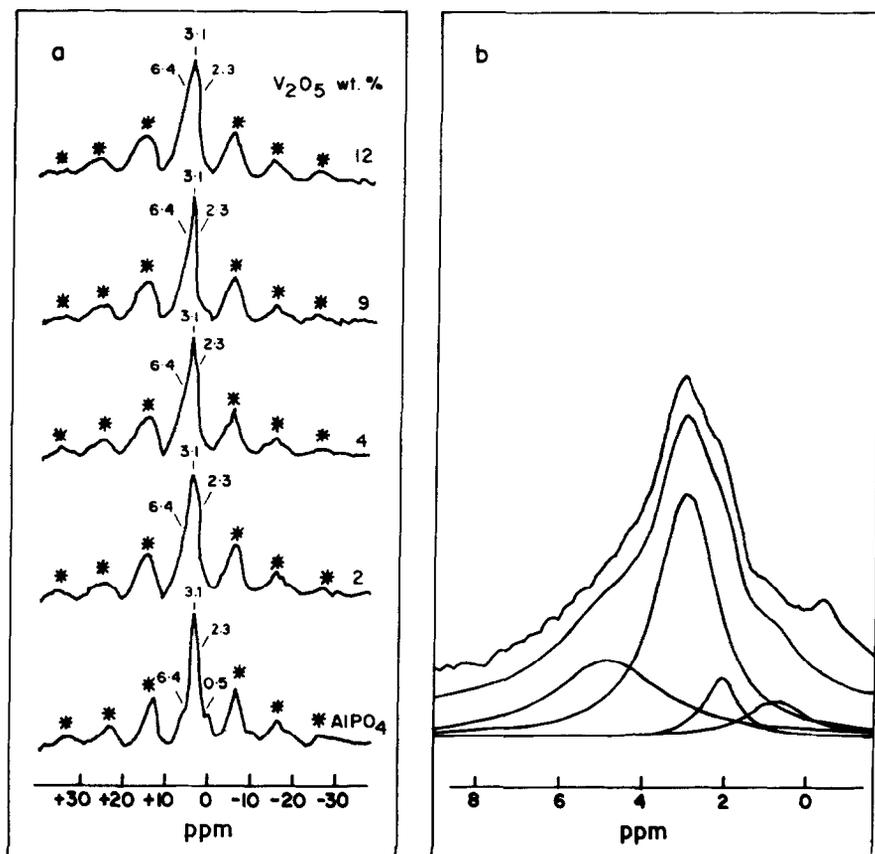


Fig. 2. (a) Solid state 1H MAS NMR spectra of the hydroxyl groups of $AlPO_4$ and $V_2O_5-AlPO_4$ catalysts. (b) Expanded spectrum of $AlPO_4$.

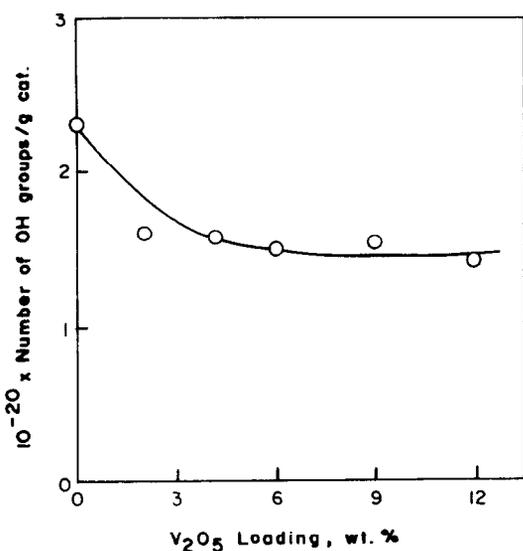


Fig. 3. Total number of hydroxyl groups plotted as a function of V₂O₅ loading.

with $\delta = 2.3$ ppm may belong to the Al–OH group coordinated to two octahedral Al atoms [26]. The total number of OH groups as a function of vanadia loading is shown in Fig. 3. The concentration of OH groups decreases with increasing V₂O₅ loading upto 6 wt.-% and then levels off with further increasing loading. This V₂O₅ loading can be considered as the monolayer capacity of the AlPO₄ support. From the fact that in supported catalysts the monolayer phase is formed by a strong chemical interaction between the OH groups of the support surface and the supported metal oxide precursors present in the impregnating solution, it may be inferred that the drop in surface concentration of OH groups upon deposition of vanadium oxide and then its leveling off at and beyond a certain loading (Fig. 3) provides evidence for interaction between the surface OH groups of the AlPO₄ support and the active species until completion of the monolayer. However, the smaller extent of decrease in the ¹H NMR signal intensity for V₂O₅–AlPO₄ catalysts with increasing V₂O₅ wt.-% may be due to the lack of all OH groups to interact because some of them may be present in closed pores or interior of the structure. This means that only a part of the total OH groups can be attributed to

the surface OH groups. These results are similar to those found earlier on V₂O₅–SiO₂ [27] and V₂O₅–SnO₂ [28] catalyst systems.

Taking into consideration 0.09 wt.-% V₂O₅ as the estimated amount of vanadia needed per m² of support surface to form a complete monolayer [29], the monolayer capacity of 6 wt.-% V₂O₅ for amorphous AlPO₄ (63 m² g⁻¹ BET surface area) obtained from the quantitative ¹H MAS NMR study of V₂O₅–AlPO₄ catalysts is close to theoretical monolayer capacity. This is a very significant observation from this study. The amount of V₂O₅ necessary to form a monolayer depends on the specific surface area of the system under consideration.

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