

Characterization of vanadium-containing catalysts by ^{51}V solid-state NMR

Spectroscopic background: ^{51}V nuclei have a spin of $I = 7/2$ and a quadrupole moment of $Q = -5.2 \times 10^{-30} \text{ m}^2$. Therefore, ^{51}V NMR signals of vanadium atoms in solids are affected by quadrupolar interactions. Due to the large electron valence shells of vanadium atoms, the anisotropic chemical shielding is an additional strong solid-state interaction. The ^{51}V isotope has a natural abundance of 99.75 % and a sensitivity of 0.38 in comparison with ^1H nuclei (1.0), making this isotope a suitable candidate for NMR studies of solids. For basic principles of solid-state NMR, see lectures “Solid-State NMR Spectroscopy” for Bachelor students or PhD seminars, accessible via the link “Lectures for Students”.

Vanadium phosphates, such as **vanadyl orthophosphates (VOPO_4)** and vanadyl pyrophosphate ($(\text{VO})_2\text{P}_2\text{O}_7$) **containing V^{5+} and V^{4+} species**, respectively, are important materials utilized as catalysts in heterogeneous catalysis. While **V^{5+} species are diamagnetic** and accessible for ^{51}V solid-state NMR, the **V^{4+} species are paramagnetic** and accessible in an indirect manner only via ^{31}P solid-state NMR of phosphorus atoms in the direct vicinity of the V^{4+} species (see e.g. Fig. 4 in Ref. [1]). ^{51}V solid-state NMR signals in the spectra of V^{5+} -containing solids may be characterized by **chemical shift anisotropies $\Delta\delta_{\text{cs}}$ of up to 1000 ppm**, which requires an increased effort by the identification of the central line in MAS NMR spectra. The **strength of the quadrupolar interactions of V^{5+} species, on the other hand, is weak to moderate** (see e.g. Table 1 [1] and Table 5 in Ref. [2]).

Material	δ_{iso} (ppm)	$\Delta\delta_{\text{cs}}$ (ppm)	η_{cs}	C_{Q} (MHz)	η_{Q}
$\alpha_{\text{II}}\text{-VOPO}_4$	-776	582	0.67	0.83	0.52
	-755	992	0.08	0.63	0.09
$\gamma\text{-VOPO}_4/1$	-755	955	0.15	0.55	0.68
$\gamma\text{-VOPO}_4/2$	-739	942	0.07	1.32	0.55
$\beta\text{-VOPO}_4$	-755	818	0.00	1.99	0.59
	-735	818	0.05	1.45	0.44
$\alpha_{\text{I}}\text{-VOPO}_4$	-691	820	0.00	1.55	0.55
20VPO/SBA-15	-693	830	0.07	1.99	0.71
60VPO/SBA-15	-737, -764	900	0.10	1.99	0.59

Table 1

As an example, ^{51}V MAS NMR spectra of an activated V^{5+} -containing VPO catalyst, grafted on mesoporous SBA-15 material (60 wt.-% VPO), are shown in **Fig. 1** [1]. The catalyst activation was performed in dry synthetic air at $T = 678$ K for 15 h with a subsequent sample transfer into the MAS NMR rotor without air contact (from the sealed reactor inside a glove box). For obtaining evaluable sideband patterns and for assigning the MAS central line, these spectra were recorded with sample spinning rates of $\nu_{\text{rot}} = 6.5$ kHz, 8.0 kHz, 10.0 kHz, as well as 30.0 kHz. The spectra are a superposition of the patterns of different compounds with isotropic chemical shifts (δ_{iso} values in **Table 1**) of $\delta_{51\text{V}} = 737$ ppm and 765 ppm. Comparison of the NMR spectroscopic data obtained for the activated 60VPO/SBA-15 catalysts with those of the reference materials in **Table 1** indicates that the NMR observable V^{5+} species correspond to those of $\alpha_{\text{II}}\text{-}$ and $\beta\text{-VOPO}_4$ phases [1].

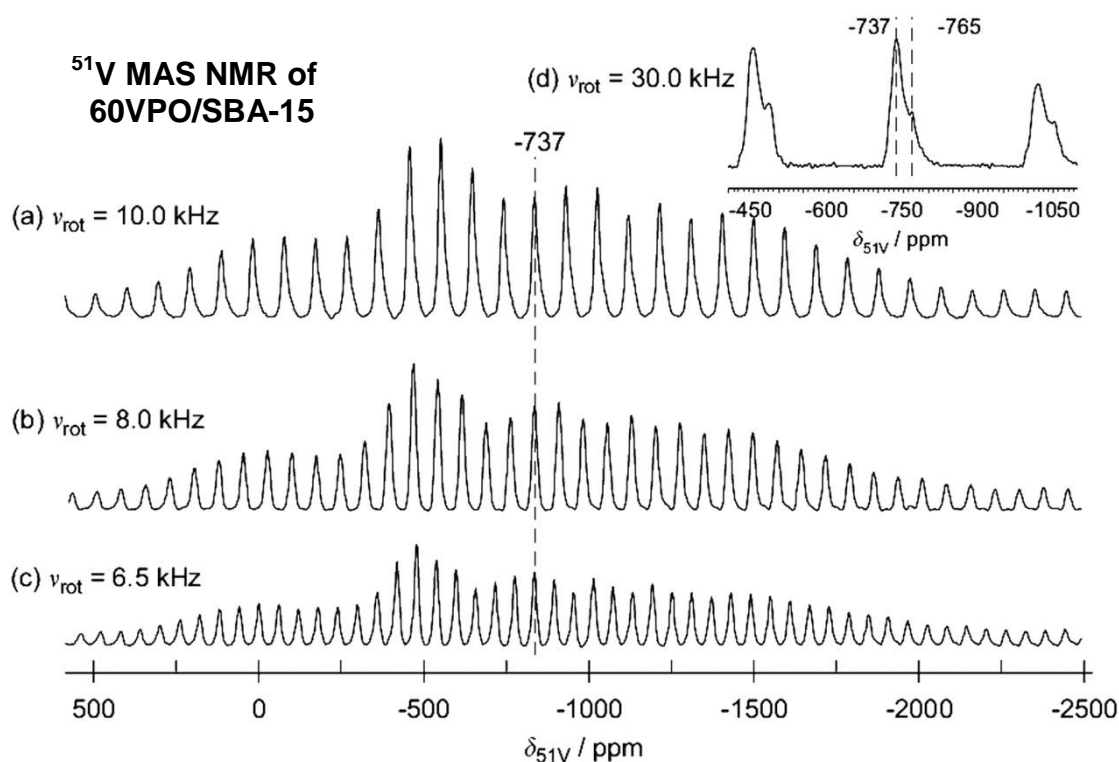
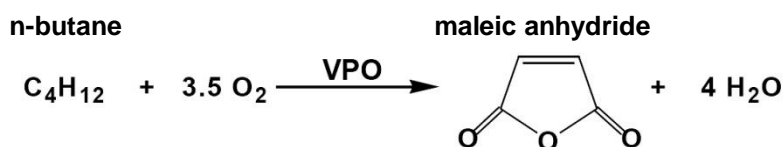


Fig. 1

In the industrial chemistry, **VPO catalysts** are utilized for the **selective oxidation of n-butane to maleic anhydride (MA)** with a maximum MA yield of 65% and an n-butane conversion of maximum 85% (**Scheme 1**) [1]. In this case, the oxygen atoms incorporated into n-butane are delivered by the V^{5+} -containing vanadyl



Scheme 1

orthophosphates (VOPO_4). For omitting total oxidation of n-butane to CO_2 , there is no oxygen in the gas phase at this reaction step. This so-called selective oxidation step transforms the V^{5+} -containing vanadyl orthophosphates (VOPO_4) into V^{4+} -containing vanadyl pyrophosphate ($(\text{VO})_2\text{P}_2\text{O}_7$). After the selective oxidation of n-butane to maleic anhydride, the n-butane flow is stopped and the catalyst is reoxidized to vanadyl [3]. In **Fig. 2**, the conversion X of n-butane (\bullet), the selectivity S to maleic anhydride (\circ), the yield Y of maleic anhydride (\triangle), and the V^{4+} -sensitive UV/Vis absorption at ca. 400 nm (\blacktriangle) are plotted for the selective oxidation of n-butane on 60VPO/SBA-15 at $T = 678 \text{ K}$. This catalysis was performed using synthetic air loaded with n-butane in the periods assigned 'O₂' or nitrogen loaded with n-butane in the periods assigned 'no O₂' [3].

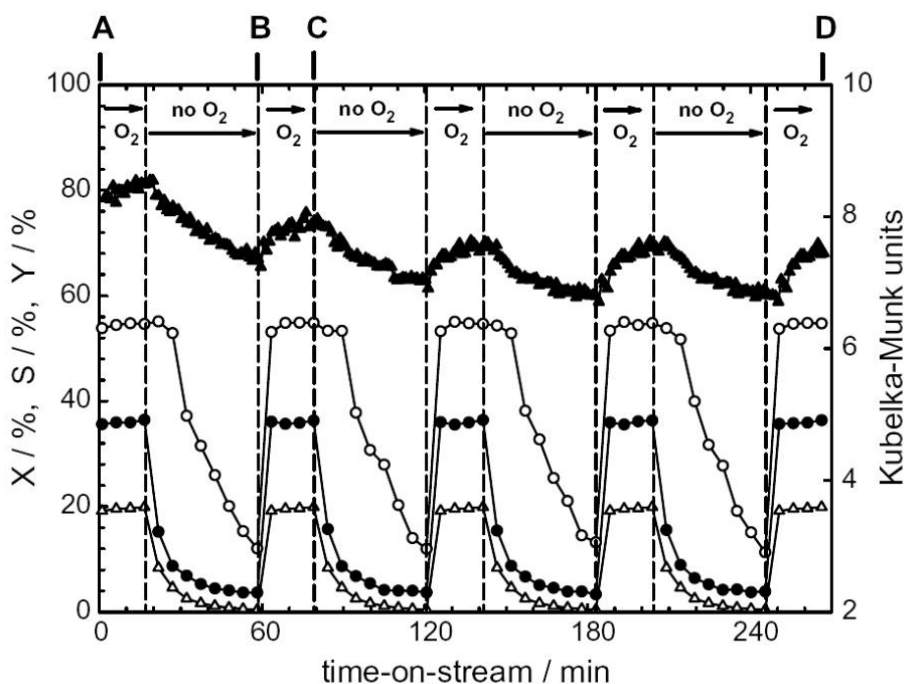


Fig. 2

In **Fig. 3**, the ^{51}V MAS NMR spectra of catalyst samples are depicted, which were taken without air contact (*vide supra*) at the reaction times **A**, **B**, **C**, and **D**, marked in

Fig. 2 [3]. While the signal at $\delta_{51V} = 735$ ppm dominates the spectra of sample **A**, this signal disappears in the spectra of sample **B** and appears again as weak signals in the spectra of samples **C** and **D**. The signal at $\delta_{51V} = 770$ ppm exists also in the spectra of the completely reduced sample **B** and shows a weak increase in the spectra of samples **C** and **D**. The comparison of the 51V MAS NMR spectra of the VPO/SBA-15 samples **A** to **D** indicates a strong decrease of the signal intensities upon reduction of the activated catalyst (sample **A** \rightarrow sample **B**) and a

51V MAS NMR of 60VPO/SBA-15

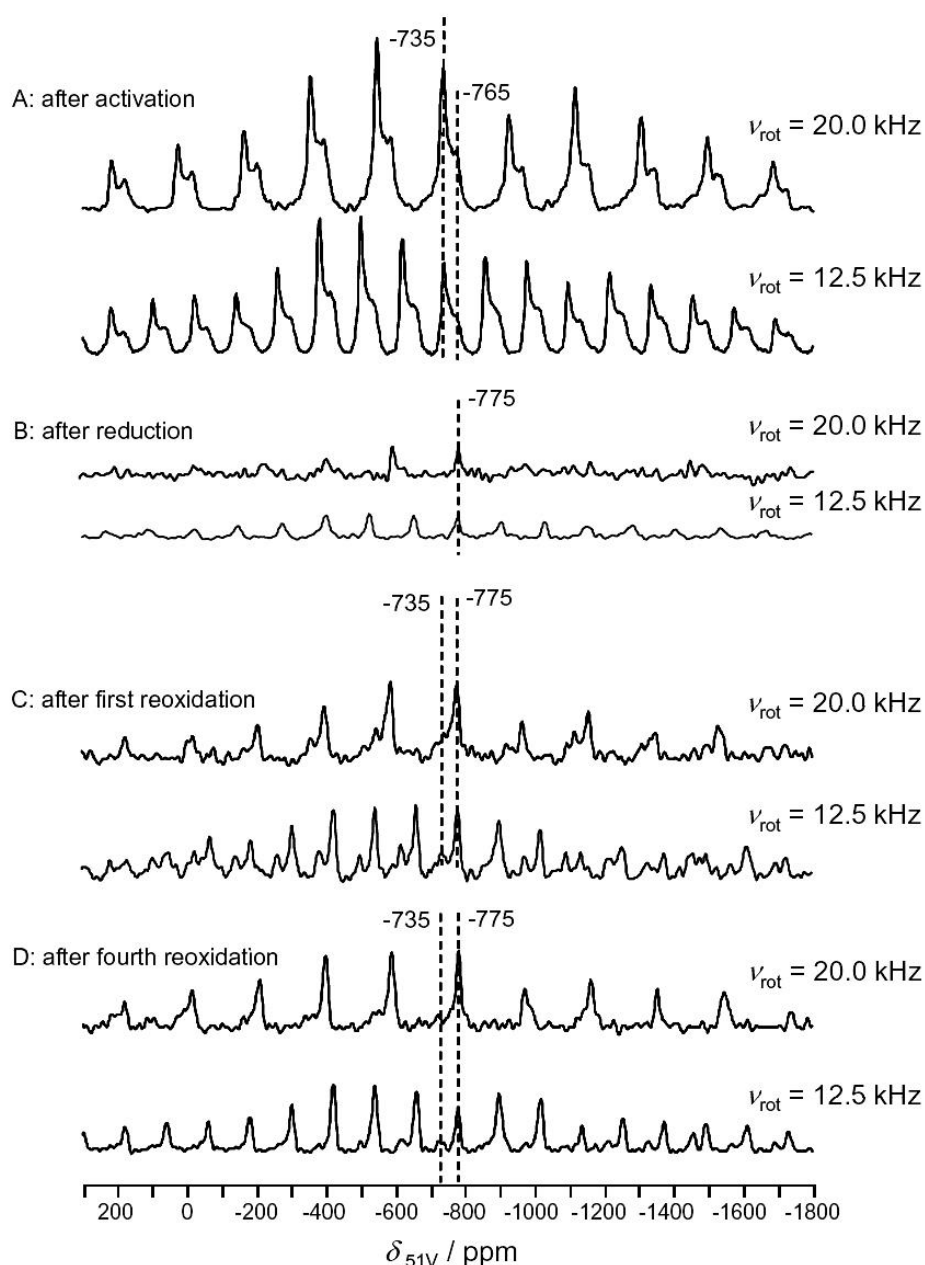


Fig. 3

significant increase of the intensities after reoxidation (sample **B** → sample **C** and sample **D**). Hence, the changes in the total intensities of the ^{51}V MAS NMR signals are due to the transformation of V^{5+} into V^{4+} species and *vice versa*. The assignments of the ^{51}V MAS NMR signals in **Fig. 3** correspond to those for the spectra in **Fig. 1** (*vide supra*).

For further ^{51}V solid-state NMR studies of vanadium-containing solid catalysts, see Refs. [2] and [4-8].

Catalyst preparation: The synthesis and activation of the VPO/SBA-15 samples were performed as described elsewhere [1, 3]. After their activation or catalytic application, these samples were transferred into the MAS rotors without contact to air in a mini glove box (see Section “mini glove box”, accessible via the link “*In Situ* Solid-State NMR Techniques”) purged with dry nitrogen gas.

^{51}V solid-state NMR studies: The ^{51}V MAS NMR spectra were recorded using 4 mm and 2.5 mm MAS NMR probes, at the resonance frequency of $\nu_0 = 105.25$ MHz, using single pulse excitation of $0.61 \mu\text{s}$ ($\pi/8$), and with the repetition time of 0.5 s. Due to the distribution of the signal intensities over broad MAS NMR sideband patterns, 16000 free induction decays were collected for each spectrum. Chemical shifts are referenced to vanadinite ($\delta_{^{51}\text{V}} = -507.7$ ppm).

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