

## Characterization of vanadium-containing catalysts by $^{51}\text{V}$ solid-state NMR

**Spectroscopic background:**  $^{51}\text{V}$  nuclei have a spin of  $I = 7/2$  and a quadrupole moment of  $Q = -5.2 \times 10^{-30} \text{ m}^2$ . Therefore,  $^{51}\text{V}$  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  $^{51}\text{V}$  isotope has a natural abundance of 99.75 % and, in this state, a sensitivity of 0.38 in comparison with  $^1\text{H}$  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”.

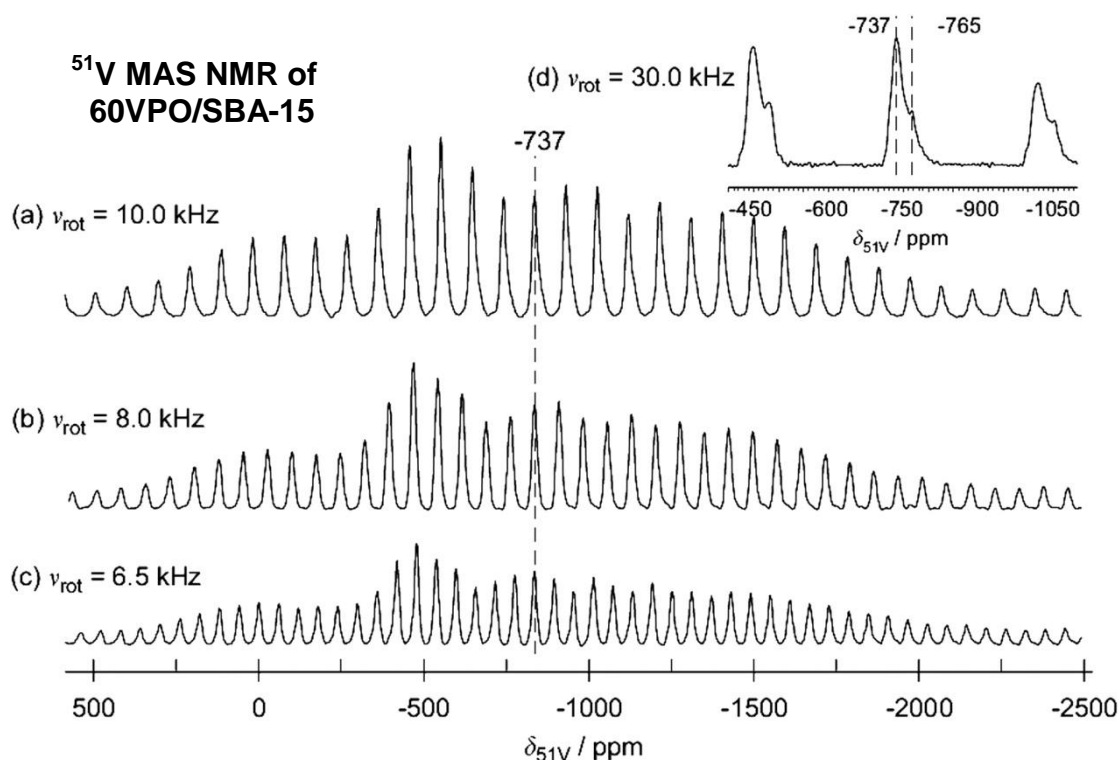
Vanadium phosphates, such as **vanadyl orthophosphates ( $\text{VOPO}_4$ )** and **vanadyl pyrophosphate ( $(\text{VO})_2\text{P}_2\text{O}_7$ )** containing  **$\text{V}^{5+}$**  and  **$\text{V}^{4+}$**  species, respectively, are important materials utilized as catalysts in heterogeneous catalysis. While  **$\text{V}^{5+}$  species are diamagnetic** and accessible for  $^{51}\text{V}$  solid-state NMR,  **$\text{V}^{4+}$  species are paramagnetic** and accessible in an indirect manner only, e.g. via  $^{31}\text{P}$  solid-state NMR of phosphorus atoms in the direct vicinity of the  $\text{V}^{4+}$  species (see Fig. 4 in Ref. [1]).  $^{51}\text{V}$  solid-state NMR signals in the spectra of  $\text{V}^{5+}$ -containing solids may be characterized by **chemical shift anisotropies  $\Delta\delta_{51\text{V},\text{cs}}$  of up to 1000 ppm**, which requires an increased effort by the identification of the MAS central line in MAS NMR spectra. The **strength of the quadrupolar interactions of  $\text{V}^{5+}$  species, on the other hand, is weak to moderate** (Table 1 and Table 5 in Ref. [2]).

Materials	$\delta_{51\text{V},\text{iso}} / \text{ppm}$	$\Delta\delta_{51\text{V},\text{cs}} / \text{ppm}$	$\eta_{51\text{V},\text{cs}}$	$C_Q / \text{MHz}$	$\eta_Q$	Refs.
$\text{V}_2\text{O}_5$	-609	645	0.11	0.80	0.00	[9]
	-609	620	0.15	0.81	0.04	[10]
$\alpha_{\text{II}}\text{-VOPO}_4$	-776	582	0.67	0.83	0.52	[2, 8]
	-755	922	0.08	0.63	0.09	[2, 6]
$\gamma\text{-VOPO}_4/1$	-755	855	0.15	0.5	0.68	[2, 8]
$\gamma\text{-VOPO}_4/2$	-739	942	0.07	1.32	0.55	[2, 8]
$\beta\text{-VOPO}_4$	-755	818	0.00	1.99	0.59	[2, 8]
	-735	818	0.05	1.45	0.44	[2, 6]

$\alpha_I$ -VOPO <sub>4</sub>	-691	820	0.00	1.55	0.55	[2, 6]
20VPO/SBA-15	-693	830	0.07	1.99	0.71	[1]
60VPO/SBA-15	-737, -764	900	0.10	1.99	0.59	[1]

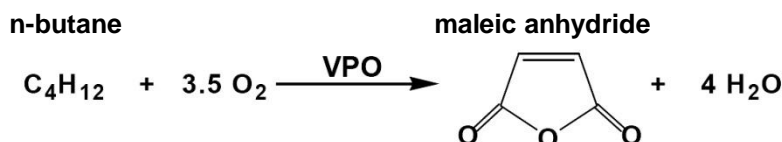
**Table 1**

As an example,  $^{51}\text{V}$  MAS NMR spectra of an activated  $\text{V}^{5+}$ -containing VPO catalyst, grafted on mesoporous SBA-15 material (60 wt.-% VPO, denoted 60VPO/SBA-15), 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 ( $\delta_{^{51}\text{V},\text{iso}}$  values in **Table 1**) of  $\delta_{^{51}\text{V},\text{iso}} = 737$  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  $\text{V}^{5+}$  species correspond to those of  $\alpha_{\text{II}}$ - and  $\beta$ -VOPO<sub>4</sub> phases [1].



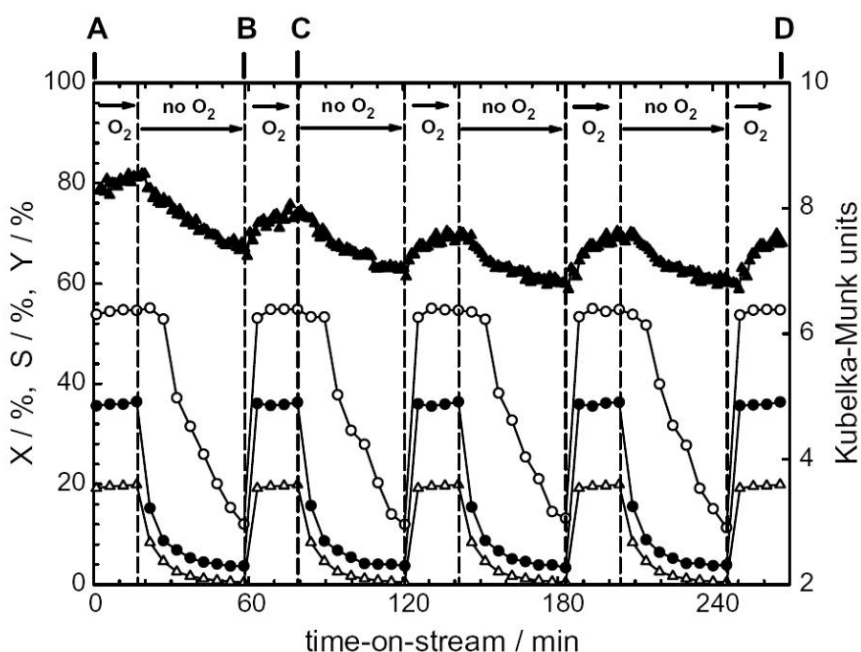
**Fig. 1**

In the industrial chemistry, **vanadium phosphate oxide (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 up to 85% (**Scheme 1**) [1]. In this case, the oxygen atoms incorporated into n-butane are delivered by the  $V^{5+}$ -



**Scheme 1**

containing vanadyl orthophosphates ( $\text{VOPO}_4$ ). For omitting total oxidation of n-butane to  $\text{CO}_2$ , 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 ( $\text{VOPO}_4$ ) 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 by purging with gaseous oxygen at elevated temperatures [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

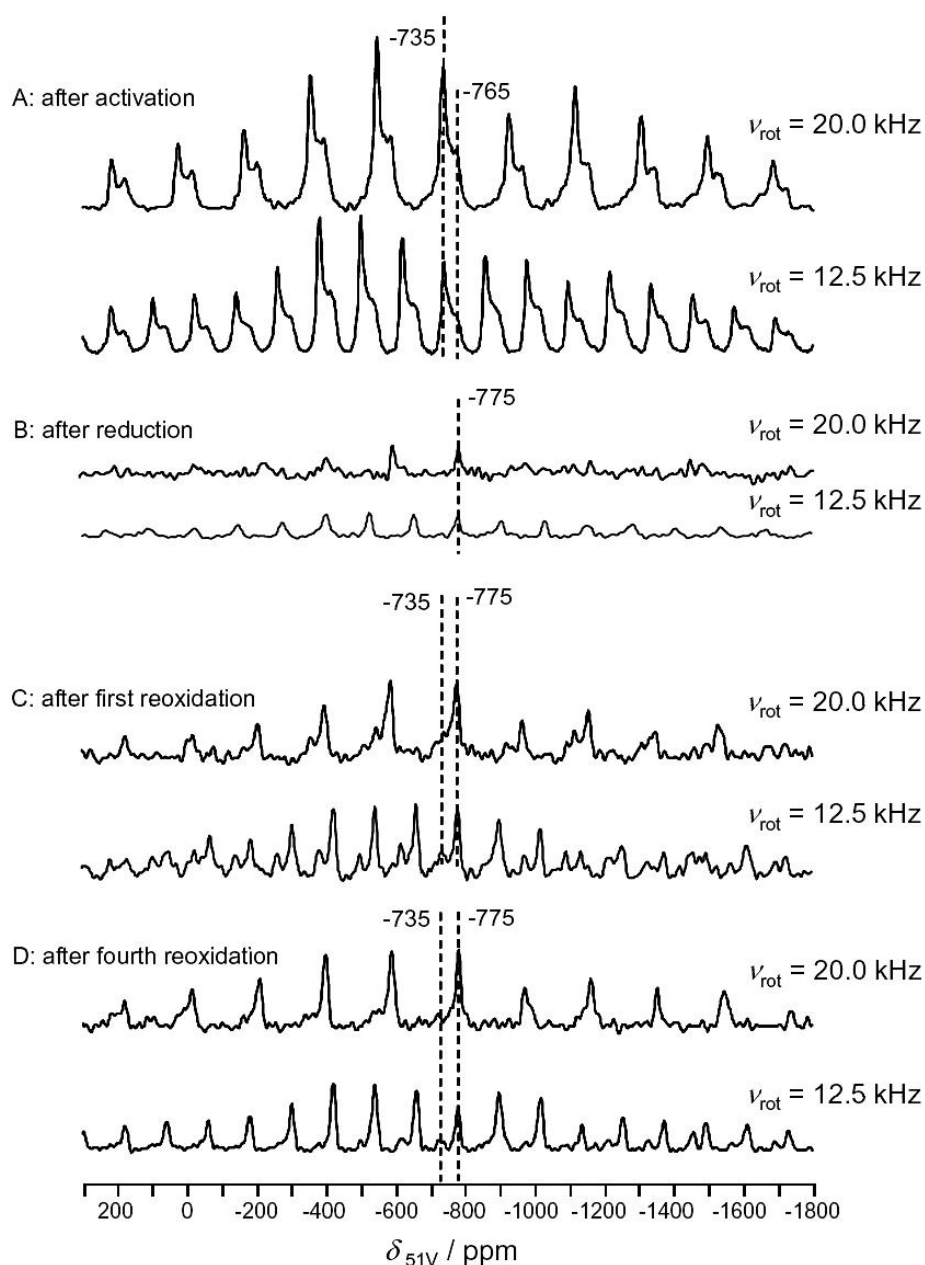


**Fig. 2**

n-butane on 60VPO/SBA-15 at  $T = 678$  K. This catalytic study was performed using synthetic air or nitrogen loaded with n-butane in the periods assigned 'O<sub>2</sub>' and 'no O<sub>2</sub>', respectively [3].

In **Fig. 3**, the <sup>51</sup>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

### <sup>51</sup>V MAS NMR of 60VPO/SBA-15



**Fig. 3**

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 60VPO/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 significant increase of the intensities after reoxidation (sample **B**  $\rightarrow$  sample **C** and sample **D**). Hence, the changes in the total intensities of the  $^{51V}$  MAS NMR signals are due to the transformation of  $V^{5+}$  into  $V^{4+}$  species and *vice versa*. The assignments of the  $^{51V}$  MAS NMR signals in **Fig. 3** correspond to those for the spectra in **Fig. 1** (*vide supra*). For further  $^{51V}$  solid-state NMR studies of vanadium-containing solid catalysts, see Refs. [2] and [4-8].

**Catalyst preparation:** The synthesis and activation of the 60VPO/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 air contact 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.

**$^{51V}$  solid-state NMR studies:** The  $^{51V}$  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  $0.61 \mu s$  ( $\pi/8$ ), 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 ( $\delta_{51V} = -507.7$  ppm).

## References:

- [1] J. Frey, Y.S. Ooi, B. Thomas, V.R. Reddy Marthala, A. Bressel, T. Schoelkopf, T. Schleid, M. Hunger, *Vanadium phosphates on mesoporous supports: Model catalysts for solid-state NMR studies of the selective oxidation of n-butane*, Solid State Nucl. Magn. Reson. 35 (2009) 130-137, DOI: 10.1016/j.ssnmr.2009.02.005
- [2] O.B. Lapina, D.F. Khabibulin, A.A. Shubin, V.V. Terskikh, *Practical aspects of  $^{51V}$  and  $^{93Nb}$  solid-state NMR spectroscopy and applications to oxide materials*, Progress in Nuclear Magnetic Resonance Spectroscopy 53 (2008) 128-191, DOI: 10.1016/j.pnmrs.2007.12.001.

- [3] J. Frey, C. Lieder, T. Schoelkopf, T. Schleid, U. Nieken, E. Klemm, M. Hunger, *Quantitative solid-state NMR investigation of  $V^{5+}$  species in VPO catalysts upon sequential selective oxidation of *n*-butane*, J. Catal. 272 (2010) 131-139, DOI: 10.1016/j.jcat.2010.03.004.
- [4] A.A. Shubin, O.B. Lapina, V.M. Bondareva, *Characterisation of strongly bonded V(V) species in  $VO_x/TiO_2$  catalyst by static and MAS solid-state  $^{51}V$  NMR spectroscopy*, Chem. Phys. Lett. 302 (1999) 341-346, DOI: 10.1016/S0009-2614(99)00103-7.
- [5] A.A. Shubin, O.B. Lapina, D. Courcot, *Characterization by solid state  $^{51}V$  NMR spectroscopy*, Catal. Today 56 (2000) 379-387, DOI: 10.1016/S0920-5861(99)00298-9.
- [6] O.B. Lapina, D.F. Khabibulin, A.A. Shubin, V.M. Bondareva,  *$^{51}V$  and  $^{31}P$  NMR studies of  $VO_x/TiO_2$  catalysts modified by phosphorous*, J. Mol. Catal. A: Chemical 162 (2000) 381-390, DOI: 10.1016/S1381-1169(00)00305-8.
- [7] O.B. Lapina, A.A. Shubin, D.F. Khabibulin, V.V. Terskikh, P.R. Bodart, J.-P. Amoureux, *Solid-state  $^{51}V$  NMR for characterization of vanadium-containing systems*, Catal. Today 78 (2003) 91-104, DOI: 10.1016/S0920-5861(02)00299-7.
- [8] R. Siegel, N. Dupre, M. Querton, J. Hirschinger,  *$^{51}V$  magic angle spinning NMR in  $VOPO_4$  phases*, Magn. Reson. Chem. 42 (2004) 1022-1026, DOI: 10.1002/mrc.1485.
- [9] J. Skibsted, N.C. Nielsen, H. Bildsøe, H.J. Jakobsen,  *$^{51}V$  MAS NMR spectroscopy: determination of quadrupole and anisotropic shielding tensors, including the relative orientation of their principal-axis systems*, Chem. Phys. Lett. 188 (1992) 405-412, DOI: 10.1016/0009-2614(92)80838-3.
- [10] C. Fernandez, P. Bodart, J.-P. Amoureux, *Determination of  $^{51}V$  quadrupole and chemical shift tensor orientations in  $V_2O_5$  by analysis of magic-angle spinning nuclear magnetic resonance spectra*, Solid State Nucl. Magn. Reson. 3 (1994) 79-91, DOI: 10.1016/0926-2040(94)90026-4.