Figure S1. FTIR-PAS spectra of the as-synthesised (non-calcined) TCV samples.

The band around 955-965 cm\(^{-1}\) increases with increasing vanadium content, strongly indicating the presence of framework incorporated vanadium. Although this band could be attributed to incorporated vanadium, the same controversy as for the calcined materials remains in case of the non-calcined samples. Since the band assignment at around 960 cm\(^{-1}\) can not unambiguously prove true incorporation of vanadium ions in framework positions. Indeed, also the intensity of the vacant T-sites that have similar band positions can cause the increase of the band at around 960 cm\(^{-1}\) since an increased amount of defect Si-O\(^{-}\) groups at higher vanadium concentrations is very likely.
Figure S2. Raman spectra of (a) TC; (b) TCV₃.₄ and (c) TCV₄.₀

Figure S3. Effects of sample ageing during ~10 months on (a) TCV₃.₄ (before (black) and after (red) ageing), (b) VO(acac)₂ / MCM-41 before ageing, (c) VO(acac)₂/MCM-41 after ageing.
We see a clear effect of ageing on the VO(acac)$_2$/MCM-41 EPR spectrum, similar to what was observed after dehydration under dynamic vacuum (Figure 5, main text). In contrast, the TCV samples do not show pronounced ageing effects.

**Figure S4.** Black: W-band ESE-detected EPR spectra of TCV$_{3,4}$ taken at 6 K. (a) $\tau = 700$ ns, (b) sum of 31 spectra whereby $\tau$ was varied from 1848 ns to 2208 ns in steps of 12 ns. $t_{\pi/2} = 140$ ns. Red top: simulation of the isolated VO$^{2+}$ center (Table 2). Bottom: simulation of the broad signal with $g = [1.995 \ 1.99 \ 1.925]$ and an EPR linewidth of 2000 MHz.

Figure S4 shows that the broad signal has a longer $T_m$ than the signal stemming from the isolated VO$^{3+}$ center.
**Figure S5.** W-band ELDOR-detected NMR spectrum of TCV3.4 taken at 6 K. (a) Observer position 3350 mT (b) Observer position 3510 mT.

In the X-band HYSCORE spectrum of TCV3.4 (Figure 7c) a cross peak stemming from a small $^{51}\text{V}$ interaction could be observed stemming from nearby V$^{5+}$ ions. The intensity of this cross peak is similar to the one found for the weak $^{29}\text{Si}$ coupling, indicating that only a small fraction of the studied VO(II) centers has a V$^{5+}$ ion in its neighborhood. Indeed, first of all the natural abundance $^{29}\text{Si}$ is 4.67 %, whereas that of $^{51}\text{V}$ is 99.75%. Moreover, $^{51}\text{V}$ has a nuclear spin 7/2, while $^{29}\text{Si}$ has only a nuclear spin of 1/2. Since the HYSCORE modulation depth (and hence the signal intensity) goes with $I(I+1)$, we can conclude that the similar HYSCORE intensities of the two cross peaks reflect that there are 450 times more Si nuclei than vanadium nuclei sitting at a distance of about 0.3-0.35 nm from a VO(II) center, or in other words, only a small fraction of the studied VO(II) centers has a V$^{5+}$ ion in its neighborhood.

Figure S5 shows the W-band ELDOR-detected NMR spectra of TCV3.4 taken at an observer position where only the broad component of the EPR spectrum contributes (S5a) and a position where the two components overlap (S5b) (see Figure S4 to locate the observer positions). A $^{51}\text{V}$ signal stemming from the surrounding V(V) ions can be observed for both cases. These signals were found to be batch dependent, reflecting some heterogeneity in the spread of the vanadium centers, and the signal depends upon the ageing time (which may be related to sample deterioration with age). The $^{29}\text{Si}$ contribution observed in the HYSCORE spectra could not be detected using the ELDOR-detected NMR method. This is most probably due to the low natural abundance of the $^{29}\text{Si}$. 

Figure S6. X-band $^1$H Mims ENDOR of TCV$_{3,4}$ recorded at 4 K at an observer position of (a) 283.8 mT (corresponding to position * in Figure 6) and (b) 294.7 mT (corresponding to position ▲ in Figure 6).

Figure S6 shows the X-band $^1$H Mims ENDOR spectra taken at different observer positions corresponding with contributions of predominantly the broad background EPR signal (S6a) or a sum of both the background and the signal corresponding from the isolated VO$^{2+}$ species (S6b) (See Figure 6, markers * and ▲). In the former case, the spectrum is dominated by the matrix proton line stemming from interactions with far away protons. In the latter case, a clear broad signal around the proton Larmor frequency is observed that stems from axial OH protons (see main text, HYSCORE).

No clear $^{29}$Si ENDOR signals could be detected at any magnetic-field setting, where they were visible in the HYSCORE spectra taken at the magnetic-field positions with the highest spin echo intensities. Although also long signal accumulations were needed to obtain these HYSCORE spectra, the ability to detect the $^{29}$Si contributions reflects the known advantage of HYSCORE (or ESEEM in general) over ENDOR to detect nuclear frequencies in the 0-10 MHz range.