Studying the environment of vanadyl complexes in the Al-Metal-Organic framework MIL-53 by a multifrequency EPR and ENDOR approach

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Introduction
- Metal Organic Frameworks (MOFs) → ordered porous materials constructed of metal ions connected by organic linkers
- Possess many attractive features → possibility of tuning the structure by varying the organic linkers or metal atoms
- Promising materials for use in catalysis, gas storage and gas separation
- MIL-47 [VO(BDC)] and MIL-53 [Al(OH)(BDC)]
- BDC = terephthalate or 1,4-benzenedicarboxylate
- MIL = Matériaux de l’Institut Lavoisier
- Possess many attractive features for use in catalysis, gas storage and gas separation
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MIL-47 vs. doped MIL-53
- Recently we reported that V-MIL-47 can be a highly selective catalyst in the liquid phase oxidation of cyclohexene[1]
- Problem: MIL-47 exhibits limited stability in aqueous environments
- Solution: Doping the highly stable MIL-53 with catalytically active V ions
- Question: Is vanadium really incorporated in the framework? → here checked for as-synthesized structures

EPR spectra at 295 K

In four figures (up) the evolution of the powder EPR spectrum with microwave frequency for as-synthesized V-doped MIL-53 at RT is shown.
The spectra are dominated by just one V\(^{4+}\) center with rhombic g and 51V hyperfine (HF) tensors whose principal axes do not coincide.

\[
\begin{align*}
g & \quad x & \quad y & \quad z \\
1.9725 & 1 & 0 & 0 \\
1.9669 & 0 & 1 & 0 \\
1.9396 & 0 & 0 & 1 \\
\end{align*}
\]

\[A\] [MHz]
\[
\begin{align*}
x & \quad y & \quad z \\
163 & 0.9686 & -0.1361 & 0.2079 \\
165 & 0.1392 & 0.9903 & 0 \\
493 & -0.2059 & 0.0289 & 0.9781 \\
\end{align*}
\]

Analysis
- Interaction with two nearest \(^{27}\)Al nuclei → \(A_1 = 0.75\) MHz and \(A_2 = 2.3\) MHz → \(d_{\text{exp}} = 3.4\) Å, \(d_1 = 3.31\) Å
- Suggesting that the \(^{51}\)V ions substitute Al in the framework

CW-ENDOR at Q-band at 10 K
- The ENDOR spectra of \(^{51}\)V in as-synthesized MIL-53 reveal HF interactions with the central \(^{51}\)V, \(^1\)H and \(^{27}\)Al nuclei

CW-ENDOR in \(^{27}\)Al range
- Interaction with two nearest \(^{27}\)Al nuclei
- \(A_1 = 3.1\)
- \(A_2 = 3.4\)
- \(A_3 = 8.6\)
- \(A_4 = 3.1\)
- \(d_{\text{exp}} = 3.4\) Å, \(d_1 = 3.31\) Å
- Suggesting that the \(^{51}\)V ions substitute Al in the framework

Field dependence ENDOR spectra in \(^1\)H range

To do: Calcined structures

References:

Acknowledgments:

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