

## Presence of Surface Vanadium Peroxo-oxo Umbrella Structures in Supported Vanadium Oxide Catalysts: Fact or Fiction?

Julie E. Molinari and Israel E. Wachs\*

*Operando Molecular Spectroscopy & Catalysis Laboratory, Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015*

Received June 20, 2010; E-mail: iew0@lehigh.edu

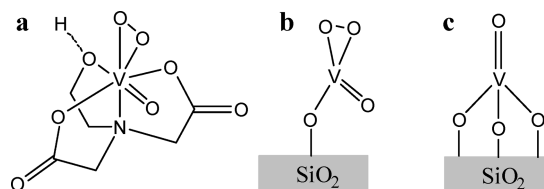
**Abstract:** Recent debates over the active site structure of supported vanadia/silica catalysts have suggested the existence of a surface vanadium peroxo-oxo “umbrella” structure. This study definitively demonstrates with Raman and UV–vis spectroscopy that the surface vanadia peroxo-oxo umbrella-like structure is not present for both hydrated and dehydrated supported vanadia catalysts such as supported vanadia on silica. The vanadia peroxo-oxo umbrella structure, however, is present in vanadium haloperoxidase (VHPOs) enzymes and metal–organic compounds designed to mimic VHPOs.

Bioinspired catalysts are finally making their debut in the world of traditional heterogeneous catalysis.<sup>1–5</sup> Such an approach to research has already been embraced in drug discovery laboratories. Rather than designing a pharmaceutical compound *de novo*, from scratch, researchers can modify a natural compound to produce a better analog.<sup>6,7</sup> In some cases it is wiser and more efficient to study the way nature performs catalysis and bring that knowledge back to our research laboratories. If nature stabilizes and optimizes the structure of a catalytic active site, then perhaps a synthetic heterogeneous catalyst would be thermodynamically stable with the same configuration for the catalytic active site.

Vanadium haloperoxidases (VHPOs) are a class of enzymes that contain a vanadium oxide cofactor in the center.<sup>8</sup> In its active form, the vanadium cofactor contains a vanadium peroxo group, a double bond oxo group, two long V–O bonds ligated to supporting amino acids, and a direct long V–N bond to a distal histidine residue.<sup>9–11</sup> VHPOs exist naturally in some algae and fungi and are thought to catalyze the oxidation of a halide to the hypohalous acid as a defense mechanism against microbes and other potentially destructive organisms.<sup>8,12,13</sup> VHPOs are being studied not only as a halide oxidant but also as a catalyst for other reactions such as sulfoxidation and alcohol oxidation.<sup>14–16</sup> In addition, VHPOs are becoming of interest to medical researchers since vanadium has been found to have therapeutic effects on diseases such as diabetes mellitus and osteosarcomas.<sup>17–19</sup>

Various research groups have designed different metal–organic compounds with the intention of mimicking the structure and function of the active peroxidated form of VHPOs.<sup>20–22</sup> The most studied mimic compound is K[VO(O<sub>2</sub>)(heida)], a vanadium peroxo-oxo compound chelated with *N*-(2-hydroxyethyl) iminodiacetic acid (heida), pictured in Figure 1a.<sup>20</sup> The K[VO(O<sub>2</sub>)(heida)] complex is a structural and functional mimic of vanadium bromoperoxidase. It is able to catalyze bromide and iodide oxidation, asymmetric sulfoxidation, and alcohol oxidations.<sup>20,23</sup>

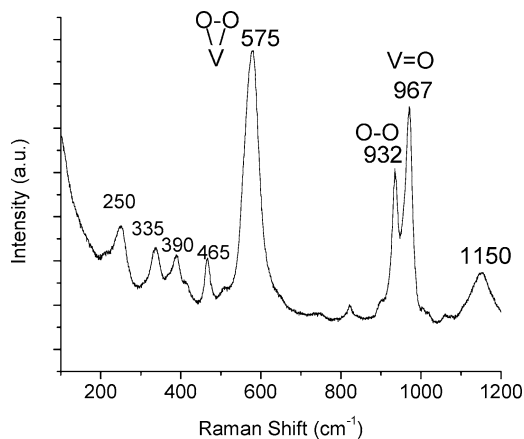
The vanadium peroxo-oxo structure has recently been proposed to be present on dehydrated supported vanadia catalysts (see Figure 1b), where it has been dubbed the vanadium oxide “umbrella”



**Figure 1.** (a) Structure of K[VO(O<sub>2</sub>)(heida)] mimic of VHPO showing peroxo and oxo groups. (b) Proposed vanadium oxide “umbrella” structure supported on silica showing the proposed peroxo-oxo groups. (c) Structure of dehydrated supported vanadia species on silica possessing the trigonal pyramid structure.

structure, based on a comparison between Density Functional Theory (DFT) results and a previously unassigned Raman band at  $\sim 920\text{ cm}^{-1}$  present for supported vanadium oxide catalysts.<sup>24</sup> The proposed vanadium peroxo-oxo structure happens to be nearly identical to the active site structure present for K[VO(O<sub>2</sub>)(heida)] shown in Figure 1a. There is no experimental evidence, however, for the existence of a stable, dehydrated surface vanadium oxide umbrella structure on an oxide support like silica. Multiple spectroscopic characterization studies have demonstrated that, at low coverage, the molecular structure of the dehydrated surface vanadium oxide species on oxide supports exists in its fully oxidized state as the VO<sub>4</sub> trigonal pyramidal structure with an apical V=O oxo and three bridging V–O–Support bonds shown in Figure 1c.<sup>25–32</sup> In addition, several groups have provided evidence that the  $\sim 920\text{ cm}^{-1}$  band is assignable to a V–O–Si vibration.<sup>33,34</sup>

Although the supported vanadium peroxo-oxo umbrella structure under dehydrated conditions has subsequently been revoked, it has been suggested that a hydrated version of the umbrella structure is still possible where the peroxo O–O moiety would instead be present as two –OH groups.<sup>35,36</sup> It has also been demonstrated that peroxo V–O<sub>2</sub> species on vanadium oxide nanoparticles are not thermally stable at the temperatures which are used to synthesize supported vanadium oxide catalysts. Surface superoxo V–O<sub>2</sub> species formed on vanadium oxide nanoparticles are only stable at temperatures until 225 K and convert to V=O groups above this temperature.<sup>37</sup> Furthermore, there are still research groups who continue to look for evidence of the dehydrated surface vanadium peroxo-oxo umbrella structure on oxide supports and seek to assign vibrational modes to the umbrella structure. Recent published DFT results concluded that the full catalytic cycle for methanol oxidation over vanadia on silica passes through a dehydrated vanadium peroxo-oxo umbrella structure upon reoxidation of the catalyst.<sup>38</sup> We intend with this communication to determine if the surface vanadium peroxo-oxo structure is truly present on oxide supports by comparing the vibrational spectrum of the umbrella structure present in K[VO(O<sub>2</sub>)(heida)] to the vibrational spectrum of supported vanadium oxide species on a silica support.<sup>25</sup>



**Figure 2.** Raman spectrum of  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]$  (aq) showing peroxo breathing mode at  $575\text{ cm}^{-1}$  in addition to O—O stretching at  $932\text{ cm}^{-1}$  and V=O stretching at  $967\text{ cm}^{-1}$ .

The Raman spectrum of aqueous  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]$ , possessing the ligated umbrella structure, is presented in Figure 2. The Raman spectrum of aqueous  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]$  exhibits four important key bands at  $575$ ,  $932$ ,  $967$ , and  $1150\text{ cm}^{-1}$ . Assignment of these bands was assisted with isotopically labeled  $\text{H}_2^{18}\text{O}_2$  and  $\text{H}_2^{18}\text{O}$ . The addition of  $\text{H}_2^{18}\text{O}_2$  during  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]$  (aq) synthesis only elicits a red shift in the vanadium O—O stretch ( $932 \rightarrow 881\text{ cm}^{-1}$ ), V—O<sub>2</sub> stretch ( $575 \rightarrow 547\text{ cm}^{-1}$ ), and its V—O<sub>2</sub> overtone ( $1150 \rightarrow 1108\text{ cm}^{-1}$ ) but not that of the band at  $967\text{ cm}^{-1}$ . The addition of  $\text{H}_2^{18}\text{O}$ , however, does not perturb the bands at  $1150$ ,  $575$ , or  $932\text{ cm}^{-1}$  but leads to a red shift of the  $967\text{ cm}^{-1}$  band that must be associated with the V=O stretch. Thus, the selective isotopic oxygen shifts confirm the vibrational assignments of  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]$  (aq).

The  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]$  (aq) signature peroxo-oxo Raman bands (V=O stretch at  $967\text{ cm}^{-1}$ , O—O stretch at  $932\text{ cm}^{-1}$ , and V—O<sub>2</sub> stretch at  $575\text{ cm}^{-1}$ ) are also present for  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]$  impregnated onto  $\text{SiO}_2$  as seen in Figure 3. The silica-supported  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]$ , however, was found to decompose after approximately 24 h and reflects its poor stability on oxide supports. The fully hydrated supported  $\text{V}_2\text{O}_5/\text{SiO}_2$  catalysts exhibit broad Raman bands at  $\sim 1020$ ,  $\sim 704$ ,  $\sim 652$ ,  $506\text{--}523$ ,  $264\text{--}274$ , and  $155\text{--}164\text{ cm}^{-1}$  that do not match those of the silica supported  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]$  complex.<sup>30</sup> The observed Raman bands for the dehydrated supported  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]/\text{SiO}_2$  are also quite different than those for dehydrated supported  $\text{VO}_4/\text{SiO}_2$  in Figure 3 with the V=O vibration at  $1035\text{ cm}^{-1}$ . The dehydrated supported  $\text{VO}_4/\text{SiO}_2$  catalyst does not contain the peroxo O—O stretch at  $\sim 930\text{ cm}^{-1}$ , the peroxo V—O<sub>2</sub> stretch at  $\sim 575\text{ cm}^{-1}$ , or the UV–vis peroxo O—O transition at  $\sim 430\text{ nm}$  (see UV–vis section below). If the dehydrated surface  $\text{VO}_4$  umbrella structure on  $\text{SiO}_2$  did indeed exist, then the peroxo V—O<sub>2</sub> stretch at  $\sim 575\text{ cm}^{-1}$ , the V-peroxo O—O stretch at  $\sim 930\text{ cm}^{-1}$ , and the peroxo O—O  $430\text{ nm}$  transition would be easily detected with Raman and UV–vis spectroscopy, respectively.

It is, therefore, concluded that an umbrella-type vanadium peroxo-oxo structure does not exist for hydrated or dehydrated supported  $\text{V}_2\text{O}_5/\text{SiO}_2$  catalysts. Examination of the Raman spectra for other supported vanadium oxide catalyst systems also reveals that the umbrella vanadium peroxo-oxo structures are not present.<sup>25</sup> The umbrella-type vanadium peroxo-oxo structure, however, is a valid model in vanadium oxide biocatalyst systems including VHPOs and mimic compounds such as  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]$ . Thus, although a protein or organic support stabilizes vanadium peroxo-oxo structures, oxide supports do not seem to stabilize the vanadium

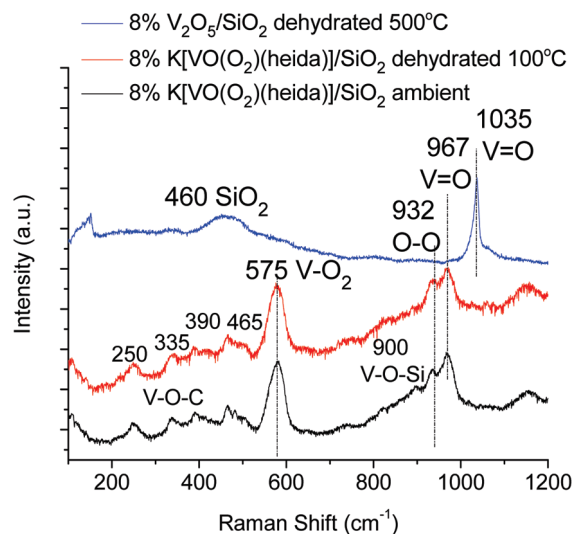
peroxo-oxo structures that have been suggested for supported vanadium oxide catalysts.

**$\text{K}[\text{VO}(\text{O}_2)(\text{heida})]$  Synthesis.** The  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]$  was synthesized according to the methods published by Colpas et al.<sup>20</sup> A 30 mL aliquot of deionized water was cooled to approximately  $0\text{ }^\circ\text{C}$  while stirring, and 5 mmol of  $\text{KVO}_3$  (Alfa Aesar, 99.9% pur.) were added and stirred until dissolved. Special care was taken so that there was no excess  $\text{KVO}_3$ . The solution was filtered, and 5 mmol of *N*-(2-hydroxyethyl)iminodiacetic acid (TCI America, min. 98% pur.) were added and stirred until completely dissolved. Then, 2 mL of 30%  $\text{H}_2\text{O}_2$  were added dropwise to yield a dark red solution. The compound was buffered to pH 4, stirred overnight, and then refrigerated at  $2\text{--}8\text{ }^\circ\text{C}$  for at least 24 h. To facilitate formation of  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]$  crystals, approximately 30 mL of 200 proof cold ethanol were added dropwise. The suspension was returned to the refrigerator for at least another 24 h until rod-shaped, dark red crystals were formed. The crystals were collected by filtration, washed with cold 200-proof ethanol, and allowed to air-dry. The  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]$  was redissolved in deionized water for aqueous spectroscopy experiments. CAUTION: Although we have never experienced any problems working with vanadium peroxo compounds, extra care should be taken when handling vanadium peroxos since closely related metal peroxo compounds have been found to be explosive.<sup>23</sup>

**UV–vis Transmission and  $^{51}\text{V}$  NMR Spectroscopy.** Transmission UV–vis and  $^{51}\text{V}$  NMR spectroscopy were used as complements to Raman spectroscopy to check the integrity of the synthesized  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]$ . The aqueous solution of  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]$  was examined using the Varian Cary 5E UV–vis spectrophotometer. First, a deionized water baseline spectrum was prepared over the range of  $200\text{--}800\text{ nm}$  under ambient conditions, and the spectrum of each aqueous catalyst sample was collected from  $200$  to  $800\text{ nm}$  under ambient conditions.

The UV–vis spectrum of  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]$  exhibits a broad absorbance band at  $\sim 430\text{ nm}$  that confirms the identity of a vanadium peroxo group and an absorbance band below  $300\text{ nm}$  that confirms the identity of an oxo group.<sup>20</sup>

Liquid phase  $^{51}\text{V}$  NMR was performed using a Bruker Avance 500 MHz NMR under ambient conditions. Aqueous  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]$



**Figure 3.** Raman spectra of supported  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]/\text{SiO}_2$  under ambient and dehydrated conditions and supported  $\text{V}_2\text{O}_5/\text{SiO}_2$  under dehydrated conditions. The peroxo breathing mode at  $575\text{ cm}^{-1}$  and O—O stretching at  $932\text{ cm}^{-1}$  are observed for supported  $\text{K}[\text{VO}(\text{O}_2)(\text{heida})]/\text{SiO}_2$  but not for dehydrated supported  $\text{V}_2\text{O}_5/\text{SiO}_2$ .

(O<sub>2</sub>)(heida)] was compared to a neat VOCl<sub>3</sub> reference standard. Liquid phase <sup>51</sup>V NMR gives rise to a single sharp band at -593 ppm, which is consistent with a peroxy-oxo coordinated vanadium.<sup>20</sup>

**Supported Catalyst Synthesis.** The supported catalysts were synthesized according to the method published by Tian *et al.*<sup>32</sup> Supported V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> was prepared by incipient wetness impregnation inside a continuously flowing N<sub>2</sub> glovebox using 2-propanol solutions of vanadium isopropoxide and dried overnight. The supported V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> catalyst was then dried at 120 °C for 1 h, 300 °C for another hour, and calcined at 450 °C for 2 h. The supported K[VO(O<sub>2</sub>)(heida)]/SiO<sub>2</sub> was prepared by incipient wetness impregnation in ambient air using an aqueous solution of K[VO(O<sub>2</sub>)(heida)]. The supported K[VO(O<sub>2</sub>)(heida)]/SiO<sub>2</sub> was then dried in ambient air for approximately 8 h and subsequently dried at 100 °C in flowing air for 1 h in order to avoid any heat related decomposition.

**Raman Spectroscopy.** Raman spectra of K[VO(O<sub>2</sub>)(heida)] and V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> were collected with a Horiba-Jobin Yvon LabRam-HR spectrometer equipped with a confocal microscope, 2400/900 grooves/mm gratings, and a notch filter. The visible laser excitation at 532 nm (green) was supplied by a Yag doubled diode pumped laser (20 mW). The scattered photons were directed and focused onto a single-stage monochromator and measured with a UV-sensitive LN<sub>2</sub>-cooled CCD detector (Horiba-Jobin Yvon CCD-3000 V). For the collection of ambient solid spectra, solid samples were spread evenly onto a glass slide. For the collection of ambient aqueous spectra, a single droplet was placed on a glass slide. Dehydrated spectra were taken using an environmental cell (Linkam T-1500) maintained below the confocal microscope and treating the samples at different temperatures under O<sub>2</sub>/He.

**Acknowledgment.** The Lehigh researchers gratefully acknowledge the support by the National Science Foundation Grant 0933294, Elizabeth Upton (Lehigh University) for assistance with K[VO(O<sub>2</sub>)(heida)] synthesis, and Curtis Schneider (Caltech) for guidance with K[VO(O<sub>2</sub>)(heida)] synthesis procedures.

## References

- Brimblecombe, R.; Koo, A.; Dismukes, G. C.; Swiegers, G. F.; Spiccia, L. *J. Am. Chem. Soc.* **2010**, *132*, 2892–2894.
- Fontecave, M.; Artero, V. *C. R. Chim.*, in press; DOI: 10.1016/j.crci.2010.01.013.
- Ruettinger, W.; Yagi, M.; Wolf, K.; Bernasek, S.; Dismukes, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 10353–10357.
- Schmid, A.; Dordick, J. S.; Hauer, B.; Kiener, A.; Wubbolds, M.; Witholt, B. *Nature* **2001**, *409*, 258–268.
- Schneider, C. J.; Penner-Hahn, J.; Pecoraro, V. L. *J. Am. Chem. Soc.* **2008**, *130*, 2712–2713.
- Beghyn, T.; Deprez-Poulain, R.; Willand, N.; Folleas, B.; Deprez, B. *Chem. Biol. Drug Des.* **2008**, *72*, 3–15.
- Paterson, I.; Anderson, E. A. *Science* **2005**, *310*, 451–453.
- Butler, A.; Walker, J. V. *Chem. Rev.* **1993**, *93*, 1937–1944.
- Messerschmidt, A.; Wever, R. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 392–396.
- Raugei, S.; Carloni, P. *J. Phys. Chem. B* **2006**, *110*, 3747–3758.
- Simons, B. H.; Barnett, P.; Vollenbroek, E. G. M.; Dekker, H. L.; Muijsers, A. O.; Messerschmidt, A.; Wever, R. *Eur. J. Biochem.* **1995**, *229*, 566–574.
- Hansen, E. H.; Albertsen, L.; Schafer, T.; Johansen, C.; Frisvad, J. C.; Molin, S.; Gram, L. *Appl. Environ. Microbiol.* **2003**, *69*, 4611–4617.
- Renirie, R.; Dewilde, A.; Pierlot, C.; Wever, R.; Hober, D.; Aubry, J. M. *J. Appl. Microbiol.* **2008**, *105*, 264–270.
- Butler, A. *Coord. Chem. Rev.* **1999**, *187*, 17–35.
- Andersson, M.; Willetts, A.; Allenmark, S. *J. Org. Chem.* **1997**, *62*, 8455–8458.
- ten Brink, H. B.; Tuynman, A.; Dekker, H. L.; Hemrika, W.; Izumi, Y.; Oshiro, T.; Schoemaker, H. E.; Wever, R. *Inorg. Chem.* **1998**, *37*, 6780–6784.
- Rehder, D. *Inorg. Chem. Commun.* **2003**, *6*, 604–617.
- Rehder, D.; Bashirpoor, M.; Jantzen, S.; Schmidt, H.; Farahbakhsh, M.; Nekola, H. *ACS Symp. Ser.* **1999**, *711*, 60–70.
- Mukherjee, B.; Patra, B.; Mahapatra, S.; Banerjee, P.; Tiwari, A.; Chatterjee, M. *Toxicol. Lett.* **2004**, *150*, 135–143.
- Colpas, G. J.; Hamstra, B. J.; Kampf, J. W.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1996**, *118*, 3469–3478.
- Butler, A.; Baldwin, A. H. *Vanadium bromoperoxidase and functional mimics*; Springer: 1997; pp 109.
- de la Rosa; Roger, I.; Clague, M. J.; Butler, A. *J. Am. Chem. Soc.* **1992**, *114*, 760.
- Smith, T. S.; Pecoraro, V. L. *Inorg. Chem.* **2002**, *41*, 6754–6760.
- Gijzeman, O. L. J.; van Lingen, J. N. J.; van Lenthe, J. H.; Tinnemans, S. J.; Keller, D. E.; Weckhuysen, B. M. *Chem. Phys. Lett.* **2004**, *397*, 277–281.
- Burcham, L. J.; Deo, G.; Gao, X.; Wachs, I. E. *Top. Catal.* **2000**, *11/12*, 85.
- Cristiani, C.; Forzatti, P.; Busca, G. *J. Catal.* **1989**, *116*, 586–589.
- Deo, G.; Eckert, H.; Wachs, I. E. *Molecular structure-reactivity relationships of supported vanadium oxide catalysts*; Symposium on Structure–Activity Relationships in Heterogeneous Catalysis - Presented before the Division of Petroleum Chemistry; American Chemical Society, Boston Meeting; American Chemical Society: Washington, DC, Boston, MA, 1990; Vol. 35, pp 16–21.
- Eckert, H.; Wachs, I. E. *J. Phys. Chem.* **1989**, *93*, 6796–6805.
- Gao, X.; Wachs, I. E. *J. Phys. Chem. B* **2000**, *104*, 1261–1268.
- Gao, X.; Bare, S. R.; Weckhuysen, B. M.; Wachs, I. E. *J. Phys. Chem. B* **1998**, *102*, 10842–10852.
- Tanaka, T.; Yamashita, H.; Tsuchitani, R.; Funabiki, T.; Yoshida, S. *J. Chem. Soc., Faraday Trans.* **1988**, *84*, 2987–2999.
- Tian, H.; Ross, E. I.; Wachs, I. E. *Quantitative J. Phys. Chem. B* **2006**, *110*, 9593–9600.
- Magg, N.; Immaraporn, B.; Giorgi, J. B.; Schroeder, T.; Bäumer, M.; Döbler, J.; Wu, Z.; Kondratenko, E.; Cherian, M.; Baerns, M.; Stair, P. C.; Sauer, J.; Freund, H. *J. Catal.* **2004**, *226*, 88–100.
- Wu, Z.; Dai, S.; Overbury, S. H. *J. Phys. Chem. C* **2010**, *114*, 412–422.
- van Lingen, J. N. J.; Gijzeman, O. L. J.; Weckhuysen, B. M.; van Lenthe, J. H. *J. Catal.* **2006**, *239*, 34–41.
- Keller, D. E.; Visser, T.; Soulimani, F.; Koningsberger, D. C.; Weckhuysen, B. M. *Vib. Spectrosc.* **2007**, *43*, 140–151.
- Guimond, S.; Abu Haija, M.; Kaya, S.; Lu, J.; Weissenrieder, J.; Shaikhutdinov, S.; Kuhlbeck, H.; Freund, H. J.; Döbler, J.; Sauer, J. *Top. Catal.* **2006**, *38*, 117–125.
- Ding, X.; Xue, W.; Ma, Y.; Zhao, Y.; Wu, X.; He, S. *J. Phys. Chem. C* **2010**, *114*, 3161–3169.

JA105392G