



AperTO - Archivio Istituzionale Open Access dell'Università di Torino

## Toward Understanding the Catalytic Synergy in the Design of Bimetallic Molecular Sieves for Selective Aerobic Oxidations

This is the author's manuscript
Original Citation:
Availability:
This version is available http://hdl.handle.net/2318/128684 since
Published version:
DOI:10.1021/ja3119064
Terms of use:
Open Access
Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use

of all other works requires consent of the right holder (author or publisher) if not exempted from copyright

(Article begins on next page)

protection by the applicable law.



# UNIVERSITÀ DEGLI STUDI DI TORINO

This is an author version of the contribution published on:

Rebecca M. Leithall, Vasudev N. Shetti, Sara Maurelli, Mario Chiesa, Enrica Gianotti, Robert Raja Toward Understanding the Catalytic Synergy in the Design of Bimetallic Molecular Sieves for Selective Aerobic Oxidations JOURNAL OF THE AMERICAN CHEMICAL SOCIETY (2013) 135 DOI: 10.1021/ja3119064

The definitive version is available at: http://pubs.acs.org/doi/abs/10.1021/ja3119064

### Towards Understanding the Catalytic Synergy in the Design

## of Bimetallic Molecular Sieves for Selective Aerobic Oxidations

Rebecca M. Leithall,<sup>†</sup> Vasudev N. Shetti,<sup>§‡</sup> Sara Maurelli,<sup>§</sup> Mario Chiesa,<sup>§</sup> Enrica Gianotti,<sup>¥§</sup> Robert Raja<sup>†\*</sup>

<sup>†</sup> School of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK

<sup>8</sup> Department of Chemistry and NIS-Centre of Excellence, University of Turin V. P. Giuria 7 – 10125 Turin, Italy

<sup>¥</sup> Dipartimento di Scienze e Innovazione Tecnologica, Centro Interdisciplinare Nano-SiSTeMI, Università del Piemonte Orientale, via T. Michel 11, I-15100, Alessandria, Italy

Supporting Information Holder

**ABSTRACT:** Structure-property correlations and mechanistic implications play an important role in the design of single-site catalysts for the activation of molecular oxygen. In this study we rationalize trends in catalytic synergy for elucidating the nature of the active site through structural and spectroscopic correlations. In particular, the redox behavior and coordination geometry in isomorphously substituted, bimetallic VTiAIPO-5 catalysts has been investigated with a view to specifically engineering and enhancing their reactivity and selectivity in aerobic oxidations. By using a combination of HYSCORE EPR and *in situ* FTIR studies, we show that the well-defined and isolated oxophilic tetrahedral titanium centers coupled with redox active  $VO^{2+}$  ions at proximal framework positions provide the loci for the activation of oxidant that leads to a concomitant increase in catalytic activity compared to analogous monometallic systems.



<u>Figure 1</u>. Schematic representation of the AlPO-5 framework where V and Ti ions have been incorporated as isomorphous replacements for  $Al^{3+}$  and  $P^{5+}$  ions, in alternating PO<sub>4</sub> and AlO<sub>4</sub> tetrahedra.

It has been widely recognized that tetrahedrally coordinated Ti(IV) centers in titanium silicate-1 (TS-1) and Ti-MCM-41 possess well-defined, single-sites for activating a range of hydrocarbons and aromatics using hydrogen peroxide ( $H_2O_2$ ) and alkyl hydroperoxides (e.g. tert-butyl hydroperoxide, TBHP) as oxidants.<sup>1</sup> Analogous titanium sites can also be incorporated through isomorphous substitution of T-site atoms with Ti(IV) ions in the strictly alternating PO<sub>4</sub> and AlO<sub>4</sub> tetrahedra of aluminophosphate (AlPO) molecular sieves.<sup>2</sup> The activity of these catalytic centers can be further enhanced by engineering a second, redox-active site, via simultaneous incorporation of two different transition-metal ions (e.g. Co<sup>III</sup>Ti<sup>IV</sup>AlPO-5).<sup>3</sup> Whilst this latter category of monometallic and bimetallic Ti-containing catalysts have proved effective in the oxidation of olefins using  $H_2O_2^4$  and acetylperoxyborate (APB) as oxidants,<sup>5</sup> there have been very few reports outlining their efficacy for activating molecular oxygen in selective oxidation reactions.

Engineering two cooperative components into a catalyst is often interpreted as being either support-metal synergy (for effective anchoring)<sup>6</sup> or metal-metal synergy (e.g. bifunctionality).<sup>7</sup> Alloying two metal using molecular carbonyl precursors affords bimetal-lic nanoparticle catalysts (e.g. Pd-Ru<sup>8</sup> or Pt-Ru<sup>9</sup>) that exhibit considerable synergy in catalytic hydrogenations. The origin of the catalytic synergy in the Pd<sub>6</sub>Ru<sub>6</sub> bimetallic cluster catalysts has been attributed to the ruthenium sites activating molecular hydrogen with the concomitant activation of the olefinic bond by palladium atoms; whilst Adams et al<sup>8</sup> have found explicit evidence that the Pt-Ru bonds are directly implicated in the catalytic hydrogenation of alkynes. Oxophiles such as antimony, bismuth and tin, when alloyed with suitable metals such as rhenium, ruthenium and platinum generate highly dispersed nanoparticle catalysts for ammoxidation and selective hydrogenation reactions<sup>10</sup> the oxophile here plays an important role in securely anchoring the nanoparticle catalyst to the support.<sup>11</sup> In addition, it has also been shown<sup>12</sup> that ruthenium and tin active sites supported (by impregnation and deposition methods) on  $\gamma$ -alumina exhibit synergistic enhancements in both catalytic activity and selectivity: the oxophilic tetrahedral Sn sites alter the polarization of the carbonyl bonds (via Sn-O interactions) thereby facilitating Ru-H hydride transfers in the hydrogenation of cinnamaldehyde.

Whilst there is an abundance of literature for enabling such synergistic interactions using metal nanoparticles<sup>13</sup> and postsynthesis modification/impregnation techniques,<sup>14</sup> there are relatively very few examples<sup>7</sup> for generating multimetallic, isolated active sites, through simultaneous isomorphous framework substitution. In this investigation we have specifically devised a synthetic strategy where the local structural environment, redox behavior and coordination geometry of the bimetallic species (V-Ti) can be precisely controlled, so that the nature of the active site and its implicit role in the catalytic process can be ascertained through spectroscopic characterization (Diffuse Reflectance UV-Vis (DR UV-Vis), FT-IR and EPR), thereby enabling structureproperty correlations to be established. This has, in turn, facilitated the evaluation of its catalytic potential in reactions involving molecular oxygen as the oxidant, which have paved the way for exploring the potential of these materials in industrially-significant catalytic transformations from the standpoint of sustainable catalysis.

Bimetallic VTiAlPO-5 catalysts were synthesized (see SI 1 for full synthesis details) by adapting and suitably modifying previously reported procedures,<sup>3</sup> using a gel ratio of;  $0.97AI : 1.5P : 0.03M : 0.03Ti : 0.8SDA : 50H_2O$ , where M is the complementary redox metal and the SDA is N-methyl dicyclohexylamine.<sup>15</sup> For comparison, monometallic (V, Ti) and analogous bimetallic equivalents of Co<sup>III</sup>Ti<sup>IV</sup>AlPO-5 and Mn<sup>III</sup>Ti<sup>IV</sup>AlPO-5 were synthesized and their phase-purity was confirmed using powder X-ray diffraction (PXRD), that resulted in diffractograms characteristic of the AFI framework,<sup>16</sup> with a high-degree of crystallinity and with no mixed-phase impurities (see Figure SI 2.1 for patterns and Table SI 2.2 for associated Reitveld refinements). Inductively coupled plasma resonance (ICP) was used to compare the theoretical loading of the metals in the synthesis gel and the final calcined samples (refer to Tables SI 1.1 and SI 3.1). All of the metals used in this study gave a good agreement between the intended loading and the final composition, with the exception of vanadium, where  $\cong 69\%$  of the metal was incorporated into the final structure.

BET measurements gave consistent internal pore surface areas and were in good agreement with literature values.<sup>4</sup> Sample morphology was assessed using SEM (Refer to Figure SI 3.1), showing uniform spherical particles with an average size of  $10 - 20 \,\mu$ m. (See SI 3 for physical characterization data) The catalytic potential of the three bimetallic catalysts was initially evaluated in the epoxidation of cyclohexene, using reaction conditions analogous to that reported earlier<sup>3</sup> for the Co<sup>III</sup>Ti<sup>IV</sup>AIPO-5 system, with a view to establishing their comparative reactivity profile. It was indeed surprising that the VTiAIPO-5 catalyst exhibits a superior catalytic performance (over twice the conversion of cyclohexene to its epoxide – 30.5% for CoTiAIPO-5 against 63.4% for VTiAIPO-5 after 3hours. See Table SI 4.1 for full values) when compared with its analogous counterparts (Figure 2A). Acetyl peroxyborate (APB) was used as the oxidant of choice in these reactions, as redox centers (such as Mn(III) and Co(III)) are believed<sup>17</sup> to promote the formation of the active oxygen species to the reaction sphere. Moreover, the combination of this effective oxidant and the size-selectivity of the AIPO-5 channels facilitates high selectivities (in excess of 98%) towards the target cyclohexene epoxide, thereby affording the prospect to probe the origins of the enhanced turnovers in greater depth. (See Figure SI 4.3 for oxidant selectivity profiles).

In order to further substantiate the efficacy of the bimetallic substitution, we evaluated the performance of the individual (V and Ti) monometallic analogues, which were inferior to that of the bimetallic catalyst (Figure 2B). Interestingly, the performance of the physical mixture (containing identical moles of the individual monometal composition of the VTiAIPO-5 catalyst) of the two monometallic analogues is significantly lower than that of its bimetallic counterpart. This strongly suggests that the two active centers, when isomorphously incorporated into the same framework, exhibit a cooperative or synergistic influence, which facilitates an effective interaction between the substrate and oxidant, which minimizes wasteful decomposition of the latter. The heterogeneous nature of all the catalysts was scrutinized by running recycle tests (refer to SI-4) and stringently analyzing the reaction mixture (using atomic absorption spectroscopy), which revealed only minimal trace quantities (<3ppb) of metal, thereby eliminating any prospects of leaching of the active sites, which further augments the stability and recyclability of our catalysts.



Figure 2A. Comparative turnover number (TON) for the epoxidation of cyclohexene using bimetallic catalysts. Squares ( $\blacksquare$ ) VTiAlPO-5, Circles ( $\bigcirc$ ) CoTiAlPO-5, Triangles ( $\blacktriangle$ ) MnTiAlPO-5. Figure 2B. Relative performance (TON) of monometallic and bimetallic V-Ti catalysts in the the epoxidation of cyclohexene. Squares ( $\blacksquare$ ) VTiAlPO-5, Circles ( $\bigcirc$ ) monometallic VAlPO-5, Triangles ( $\bigstar$ ) monometallic TiAlPO-5, Diamonds ( $\bigcirc$ ) physical mixture of VAlPO-5 and TiAlPO-5. Catalysis carried out at 338 K, at atmospheric pressure using dichloromethane as the solvent. Oxidant : Substrate ratio 1.1:1. See SI-4 for full experimental conditions.

To elucidate the nature and role of each of the individual metal sites in the AlPO-5 catalysts, detailed spectroscopic characterization by DR UV-Vis (see Figure SI 5.1) and FT-IR spectroscopies, using CO as a probe molecule was carried out (Figure 3A). To study the redox properties of the metals (Co, V and Mn), the catalysts were reduced in  $H_2$  at 673K and subsequently oxidized in  $O_2$ at 823K.

In the UV range (270-290 nm), the VTiAlPO-5 oxidized catalyst (Fig.3A), displays an intense and broad band due to LMCT transitions of isolated  $T_d V(V)$  sites, providing direct evidence for the incorporation of V into the AlPO-5 framework. The strong tail in the 350-450 nm range suggests the presence of some polymeric vanadium species, such as  $V_2O_5$ . After reduction, the band becomes sharper with a maximum at 220-260 nm, which can be assigned to LMCT transition of monomeric V(IV) in 4- and 5-fold coordination and to Ti(IV) centres. In addition, the weak bands at 530, 660-1100 nm can be assigned to d-d transitions of  $T_d$  monomeric V(IV) centres.<sup>18</sup> In the FTIR spectra (Figure 3B), the band at 2195 cm<sup>-1</sup>, which is only detected in the reduced sample, 2

is due to CO adsorbed on vanadyl species<sup>19</sup> further substantiating that the vast majority of V(IV) sites are converted into V(V) centers upon oxidation. Detecting the titanium sites in the bimetallic-AlPO-5 catalysts was achieved by complete reduction of the catalysts in H<sub>2</sub> at 673K to eliminate the overlap of the intense UV bands of V(V) with those of Ti(IV) (inset of Fig. 3A). The VTiAlPO-5 displays a strong shoulder at 215 nm, which is attributed to isolated tetrahedral Ti(IV) LMCT transitions. The maxima at 250 nm is likely to have some contributions from both Ti(IV) and V(V) isolated sites.<sup>20</sup>

The interaction of the oxidant (APB) with the metal sites in the oxidized form was probed by *in situ* FTIR spectroscopy [v(O-O) stretching mode], in order to gain a better understanding on the nature of peroxo species formed during the catalytic reaction.<sup>21</sup> Upon interaction with APB (Figure 3C), using conditions identical to that used in the catalytic runs (reported in Figures 2A and 2B), a weak band at 884 cm<sup>-1</sup> and a broad, more intense signal at 816 cm<sup>-1</sup> were observed. The band at 884 cm<sup>-1</sup>, also present in the spectra of TiAlPO-5 and VAlPO-5, is due to physisorbed APB; whilst the broad band at 816 cm<sup>-1</sup> is assigned to the stretching mode of O-O peroxo species. This band is not present in the undoped AlPO-5 sample (see Figure SI 7.2), but is present in monometallic TiAlPO-5 and VAlPO-5, this band is centered at 816 cm<sup>-1</sup> and in VAlPO-5 at 828 cm<sup>-1</sup>, while in VTiAlPO-5 this band is broader and both components are present and can be directly attributed to peroxo-species formed on Ti(IV) and V(V) sites. Furthermore, the presence of isolated, tetrahedral Ti(IV) sites and V(V) centers in VTiAlPO-5 catalyst synergistically enhances the formation of the peroxo species, which has a beneficial effect on its overall catalytic performance (shown in Figures 2A and 2B).



Figure 3A. DR UV-Vis spectra of oxidized (blue) and reduced (red) VTiAlPO-5; the inset shows the expanded spectrum of reduced VTiAlPO-5. Figure 3B. FTIR spectra of the oxidized (blue) and reduced (red) VTiAlPO-5.recorded at 80K after CO (1 mbar) adsorption. Figure 3C. FTIR spectra of oxidized VTiAlPO-5 (red), VAlPO-5 (blue) and TiAlPO-5 (black) recorded at 80K after interaction with APB.

In order to further clarify the local environment of the Ti and V ions in the AlPO-5 framework pulse EPR experiments have been carried out on the reduced system, where both species are in their paramagnetic states (V<sup>4+</sup> and Ti<sup>3+</sup> 3d<sup>1</sup>). The Electron Spin Echo (ESE) detected EPR spectrum of the reduced VTiAlPO-5 catalyst is shown in the inset of Figure 4 and is characterized by a complex powder pattern extending over  $\approx 160$  mT and characteristic of VO<sup>2+</sup> ions in square pyramidal coordination. Superimposed to this signal a prominent absorption band characterized by a pseudo-axial **g** matrix ( $g_{\parallel}=1.991$  and  $g_{\perp}=1.908$ ) is observed, which can be firmly assigned to Ti<sup>3+</sup> species subjected to a tetrahedral crystal field<sup>22</sup> in good agreement with the UV-Vis experiments.

Hyperfine Sublevel Correlation (HYSCORE) experiments have then been carried out in order to measure the superhyperfine interactions of the unpaired electron on the metal cations with magnetically active nuclei of the AIPO lattice ( ${}^{31}P$  (*I*=1/2),  ${}^{27}AI$  (*I*=5/2)). A typical HYSCORE spectrum recorded at field positions corresponding to the maximum absorption of the Ti<sup>3+</sup> species is shown in Figure 4. The spectrum is analogous to that observed for the monometallic system (See section SI-8, Figures SI 8.2A and 8.3A) and a detailed analysis has been reported elsewhere.<sup>23</sup> The spectrum features relatively strong <sup>31</sup>P hyperfine couplings, which are indicated in Figure 4. This fact together with the absence of similar couplings to <sup>27</sup>Al nuclei, unequivocally proves that Ti<sup>3+</sup> ions are isomorphously substituted in the AIPO-5 framework at Al<sup>3+</sup> positions. Similar spectra (Figure SI 8.1) have been recorded at a field position where only VO<sup>2+</sup> species resonate, which indicate that a similar situation also holds for VO<sup>2+</sup> ions.



<u>Figure 4</u>. Experimental HYSCORE spectrum of reduced VTiAlPO-5 sample recorded at 10K and observer position  $B_0 = 362.0 \text{ mT}$  (arrow in the inset). In the inset the experimental ESE detected EPR spectrum is shown. The stick diagrams indicate the contributions of VO<sup>2+</sup> and Ti<sup>3+</sup> species to the overall signal.

From these spectroscopic observations it can be concluded that, both the vanadium and titanium centers, when isomorphously (simultaneously) incorporated into the AFI framework, play a distinct role and act in a concerted fashion for synergistically boosting the overall catalytic performance (Figure 2). The tetrahedral nature of the oxophilic titanium center is more susceptible for binding to the oxidant and activating it (through the formation of peroxo species – Figure 3C), as it is able to expand its coordination sphere, unlike the already saturated octahedral species that is observed in MnTiAlPO-5 (refer to Figure SI 5.1). It could be further rationalized that, since the complementary redox center plays a significant role in the catalytic turnover, it is evident that the vanadium ions, with a lower redox-barrier, will more efficiently catalyze the reaction once a proximal titanium center has activated the oxidant (Figure 3B). We have therefore probed the efficacy of this catalyst, in the activation of molecular oxygen, for the oxidation of benzyl alcohol and in a series of other related selective oxidations that are of high relevance in the chemical and fine-chemical industries.

The selective oxidation of benzyl alcohol to benzaldehyde is of paramount importance in the synthesis of a range of pharmaceutical intermediates (e.g. mandelic acid), plastic additives, photographic chemicals and certain aniline dyes.<sup>24</sup> Conventional industrial methods for the synthesis of vital ingredients listed in Table 1 involve the use of stoichiometric amounts of chromate, permanganate, Br<sub>2</sub>/acetic acid or TPAP/NMO (tetra-N-propylammonium perruthenate/ N-methyl-morpholine-N-oxide) as stoichiometric oxygen donors<sup>25</sup> and activators (for maximizing selectivity) which generate copious quantities of metal-waste and have serious toxicity issues associated with them.<sup>26</sup> Developing environmentally-benign, atom-efficient, sustainable, catalytic methods that, ideally utilize molecular oxygen as the oxidant for these selective transformations is therefore of vital importance from an economic and environmental viewpoint.

The catalytic results for the oxidation of benzyl alcohol, using molecular oxygen as the oxidant, for the monometallic and bimetallic VTi- catalysts are summarized in Figure 4A. In line with earlier trends, the bimetallic catalyst far exceeds the performance of its corresponding monometallic analogues, further substantiating the concerted role of the redox-active vanadium and oxophilic (tetrahedral) titanium active centers for boosting the overall efficiency of the reaction. It was noteworthy that analogous bimetallic systems with a lower degree of redox efficiency<sup>27</sup> (e.g. CoTiAlPO-5) or less-pronounced tetrahedral character (e.g. MnTiAlPO-5) were inferior in performance to the corresponding VTi-analogue (Figure 4B).





Figure 4A: Conversion (bold lines) and selectivity (dashed lines) for the aerobic oxidation of benzyl alcohol. Blue circles  $(\bullet)$ VTiAlPO-5, Red squares (■) VAlPO-5, Green triangles (▲) TiAlPO-5. Figure 4B: Comparative performance of bimetallic analogues in the aerobic oxidation of benzyl alcohol. Blue circles (●) VTiAlPO-5, Red squares (■) CoTiAlPO-5, Green triangles (▲) MnTiAlPO-5. Catalysis carried out at 373 K at 2.0 MPa of air using t-butanol as solvent. See SI-4 for full experimental conditions.

The wider scope for expanding the range of industrially-significant oxidations that could be effected with these adroitlydesigned bimetallic catalysts with molecular oxygen is further highlighted in Figure SI 4.7. Whilst further optimization of process parameters and reaction conditions is currently underway, it is remarkable that vanilly alcohol and cinnamyl alcohol were facilely oxidized using  $O_2$  as the oxidant, under rather mild conditions, displaying high catalytic turnovers (764 and 718 respectively); further substantiating the importance of the design strategy in effecting sustainable catalytic transformations both from an academic and industrial perspective.

### ASSOCIATED CONTENT

#### Supporting Information.

Additional characterization evidence and details of experimental methods can be found in the supporting information. This material is available free of charge via the Internet at http://pubs.acs.org.

#### **Corresponding Author**

\* Robert Raja, University of Southampton, rr3@soton.ac.uk

### ACKNOWLEDGMENT

The authors would like to thank Honeywell (USA) and the British Italian Partnership for funding. Matthew Potter is kindly acknowledged for his assistance with the graphical abstract.

### REFERENCES

1. (a) Wang, Y.; Wang, G.; Yang, M.; Tan, L.; Dong, W.; Luck, R., Journal of Colloid and Interface Science 2011, 353, 519 - 523; (b) Guidotti, M.; Batonneau-Gener, I.; Gianotti, E.; Marchese, L.; Mignard, S.; Psaro, R.; Sgobba, M.; Ravasio, N., Microporous and Mesoporous Materials 2008, 111, 39 -47; (c) Zahedi-Niaki, M. H.; Kapoor, M. P.; Kaliaguine, S., Journal of Catalysis 1998, 177, 231 - 239.

- Flanigen, E. M.; Lok, B. M.; Patton, L.; Wilson, S. T., Pure Appl. Chem. 1986, 58 (10), 1351-1358 2.
- 3. Paterson, J.; Potter, M.; Gianotti, E.; Raja, R., Chem. Commun., 2011, 47, 517 - 519.
- Lee, S.-O.; Raja, R.; Harris, K. D. M.; Thomas, J. M.; Johnson, B. F. G.; Sankar, G., Angewandte Chemie 2003, 115 (13), 1558-1561. 4.

5 (a) Raja, R.; Thomas, J. M.; Xu, M.; Harris, K. D. M.; Greenhill-Hooper, M.; Quill, K., Chem. Commun. 2006, 448 - 450; (b) Raja, R.; Thomas, J. M.; Greenhill-Hooper, M.; Ley, S. V.; Paz, F. A. A., Chem. Eur. J. 2008, 14, 2340 - 2348.

Hermans, S.; Raja, R.; Thomas, J. M.; Johnson, B. F. G.; Sankar, G.; Gleeson, D., Angew. Chem. Int. Ed. 2001, 40 (7), 1211 - 1215. 6.

Thomas, J. M.; Raja, R., PNAS 2005, 102, 13732 - 13736. 7.

Raja, R.; Hermans, S.; S. Shephard, D.; F. G. Johnson, B.; Sankar, G.; Bromley, S.; Meurig Thomas, J., Chemical Communications 1999, (16), 1571-8. 1572.

(a) Adams, R. D.; Captain, B., Journal of Organometallic Chemistry 2004, 689 (24), 4521-4529; (b) Adams, R. D.; Captain, B.; Zhu, L., J. Am. Chem. 9. Soc. 2004, 126, 3042.

- 10. Adams, R. D.; Blom, D. A.; Captain, B.; Raja, R.; Thomas, J. M.; Trufan, E., Langmuir 2008, 24 (17), 9223-9226.
- 11. Raja, R.; Khimyak, T.; Thomas, J. M.; Hermans, S.; Johnson, B. F. G., Angewandte Chemie International Edition 2001, 40 (24), 4638-4642.

12. Neri, G.; Mercadante, L.; Milone, C.; Pietropaolo, R.; Galvagno, S., Journal of Molecular Catalysis A: Chemical 1996, 108 (1), 41-50.

- 13. Jiang, H.-L.; Xu, Q., Journal of Materials Chemistry 2011, 21, 13705 13725.
- 14. Choudhury, I. R.; Thybaut, J. W.; Balasubramanian, P.; Denayer, J. F. M.; Martens, J. A.; Marin, G. B., Chemical Engineering Science 2010, 65, 174 -178.
- 15. Sánchez-Sánchez, M.; Sankar, G.; Simperler, A.; Bell, R. G.; Catlow, C. R. A.; Thomas, J. M., Catalysis Letters 2003, 88 (3-4), 163-167.
- 16. Figiel, P. J.; Sobczak, J. M., Journal of Catalysis 2009, 263 (1), 167-172.

17. (a) Peroxid. Chemie GMBH, US 5462692, 1995.; (b) Raja, R.; Thomas, J. M.; Xu, M.; Harris, K., D, M.; Greenhill-Hooper, M.; Quill, K., Chem. Commun., 2006, 448-450.

- 18. Vishnuvarthan, M.; Gianotti, E.; Paterson, J.; Raja, R.; Piovano, A.; Bonino, F.; Berlier, G., Microporous and Mesoporous Materials 2011, 138, 167.
- 19. Hadjiivanov, K. J.; Vayssilov, G. N., Adv. Catal. 2002, 47, 307 511.
- 20. Lenoc, L.; On, D., T.; Solomykina, S.; Echchaed, B.; Beland, F.; Moulin, C. C. D.; Bonnevoit, L., Stud. Surf. Sci. Catal. 1996, 101, 611.
- 21. Tozzola, G.; Mantegazza, M.; Ranghino, G.; Petrini, G.; Bordiga, S.; Ricchiardi, G.; Lamberti, C.; Zulian, R.; Zecchina, A., J. Catal. 1998, 179, 64 71.
- 22. Maurelli, S.; Vishnuvarthan, M.; Chiesa, M.; Berlier, G.; Van Doorslaer, S., J. Am. Chem. Soc. 2011, 133, 7340.
- 23. Maurelli, S.; Chiesa, M.; Giamello, E.; Leithall, R. M.; Raja, R., A Chem. Commun. 2012, 48, 8700 8702.
- 24. Sheldon, R., A.; van Bekkum, H., Fine Chemicals through Heterogeneous Catalysis. Wiley-VCH: Weinheim, 2001.
- 25. Backvall, J. E., Modern Oxidation Methods. Wiley-VCH: Weinheim, 2005.
- 26. Pillai, U. R.; Sahle-Demessie, E., Applied Catalysis A 2003, 245, 103 109.
- 27. (a) Berndt, H.; Martin, A.; Zhang, Y., *Microporous Materials* **1996**, *6*, 1 12; (b) Barrett, P. A.; Sankar, G.; Jones, R. H.; Catlow, C. R. A.; Thomas, J. M., J. Phys. Chem. B. **1997**, *101* (46), 9555 9562.