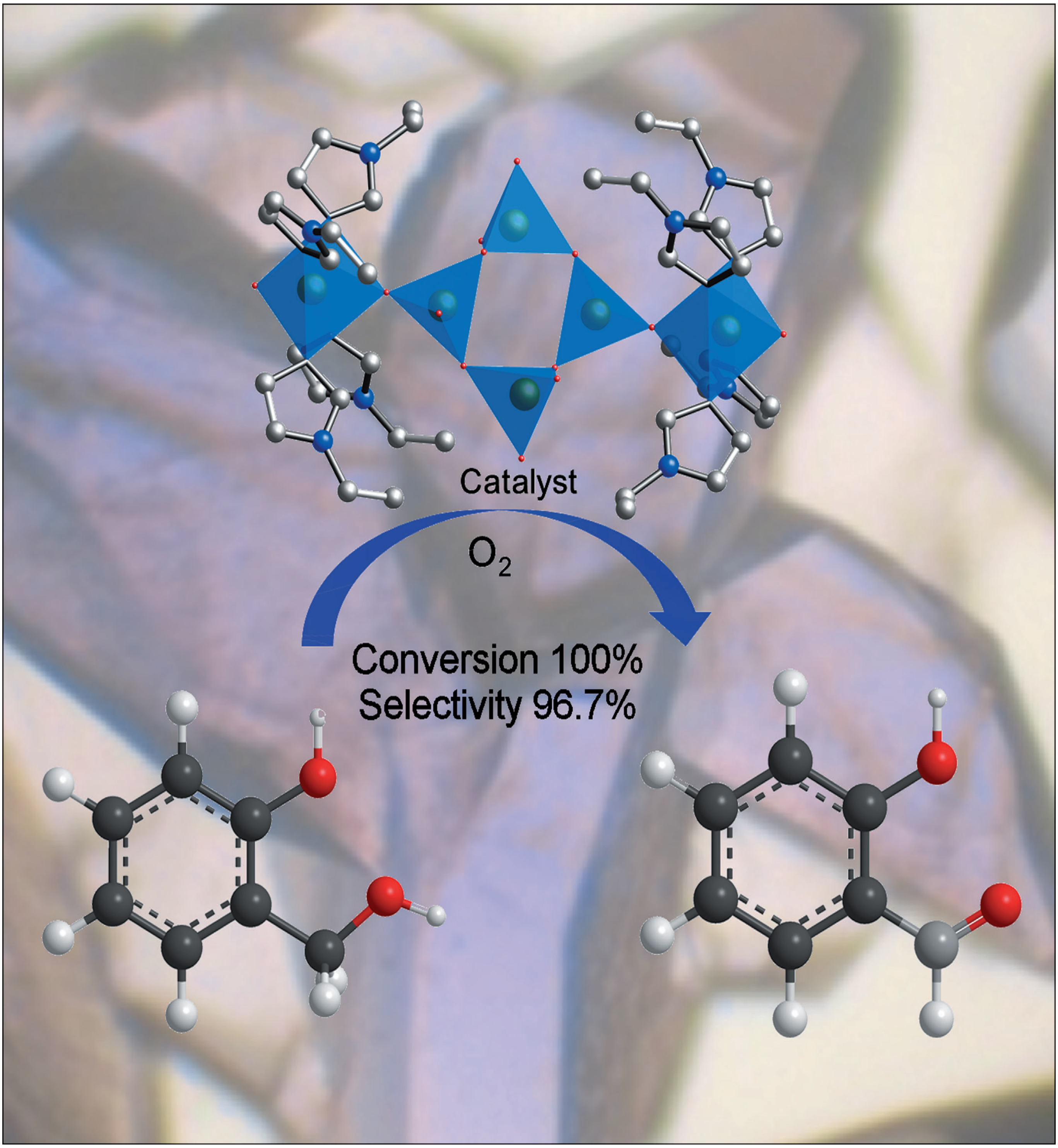
CHEMISTRY
A EUROPEAN JOURNAL

ChemPubSoc Europe

DOI: 10.1002/chem.201203854

Three New Imidazole-Functionalized Hexanuclear Oxidovanadium Clusters with Exceptional Catalytic Oxidation Properties for Alcohols

Baokuan Chen,[a] Xianqiang Huang,[a, b] Bo Wang,*[a] Zhengguo Lin,[a] Jufang Hu,[a]
Yingnan Chi,[a] and Changwen Hu*[a]



Polyoxometalates (POMs) have received great interest by virtue of their structural diversity and desirable merits in a range of applications.[1] Amongst POMs, polyoxovanadates (POVs) are of great importance due to their attractive magnetic and electronic properties, as well as their long-promised potential as oxidative catalysts.[2] Recently, a tetranuclear vanadium complex has been investigated in the catalytic oxidation systems of organic compounds with molecular oxygen as the oxidant.[3] Unlike these vanadium complexes and vanadium-substituted POMs, catalytic reactions using pure POVs are rather rare.[4] Therefore exploring synthetic methods for the preparation of new, selective, and efficient POV catalysts is essential but remains challenging.[5]

The organic-functionalized POMs based on a covalent connection can increase their solubility in organic solvents and provide a pathway to direct the substrate towards the catalytically active centers.[6] Compared with the extensive work on the organic functionalization of polyoxomolybdates and polyoxotungstates, considerably less research has been conducted in the field of POVs.[7]

Imidazole derivatives 1-R-IM (R = CH_3-, C_2H_5-, C_2H_3-, etc.) are promising candidate organic compounds as they may serve as coordination ligands, counterions, and potentially, solvents, in preparing new organic-functionalized POV structures. Herein, we present a new synthetic approach employing versatile organic compounds, 1-R-IM (R = CH_3-, C_2H_5-, C_2H_3-), and POV precursors in the assembly of neutral organic-functionalized POV clusters. In this work, three new organic functionalized POVs with imidazole ligands, $V^{V}_{6}O_{15}(mIM)_8$ (**1**), $V^{IV}_{2}V^{V}_{4}O_{14}(mIM)_8$ (**2**) and $V^{IV}_{2}V^{V}_{4}O_{14}(eIM)_8$ (**3**) (mIM: 1-methylimidazole and eIM: 1-ethylimidazole) have been synthesized by a facile solvothermal method, in which the corresponding imidazoles are employed as organic solvents. Neutral hexanuclear vanadium clusters, V_6O_{15}, as in **1**, and mixed-valence V_6O_{14}, as in **2** and **3**, are constructed with nitrogen atoms from imidazoles coordinating to POV skeletons. All compounds have been fully characterized by surface X-ray diffraction (SXRD), powder (P)XRD, FT-IR, ESR, XPS, EA, and TGA. Compound **3** was further investigated as a catalyst for the oxidative dehydrogenation of alcohols with O_2 as an oxidant.

The treatment of $NH_4V^VO_3$ with 1-mIM at 90 °C for 3 days afforded light-yellow crystals of imidazole-functionalized compound **1**. All of the vanadium atoms in **1** are in the +5 oxidation state, as revealed from the BVS calculation and XPS. SXRD shows that the structure of **1** is an isolated neutral cluster. As illustrated in Figure 1 a, the hexanuclear vanadium cluster has two V atoms in distorted [VO_4] tetrahedra and the other four V atoms in distorted [VO_3N_2] trigonal bipyramids with a τ parameter of 0.651 and 0.619.[8] We and others have reported hexanuclear vanadium clusters with Lindqvist,[9] Anderson,[10] cyclic, and other structure topologies by using alkoxo and N-containing ligands.[11] However, compound **1** shows an unprecedented open-claw-like structure that differs from the above reported oxovanadium clusters. Notably, the charge neutrality and the addition of organic ligands in **1** may enhance its solubility, which opens new avenues for homogeneous catalysis.[12]

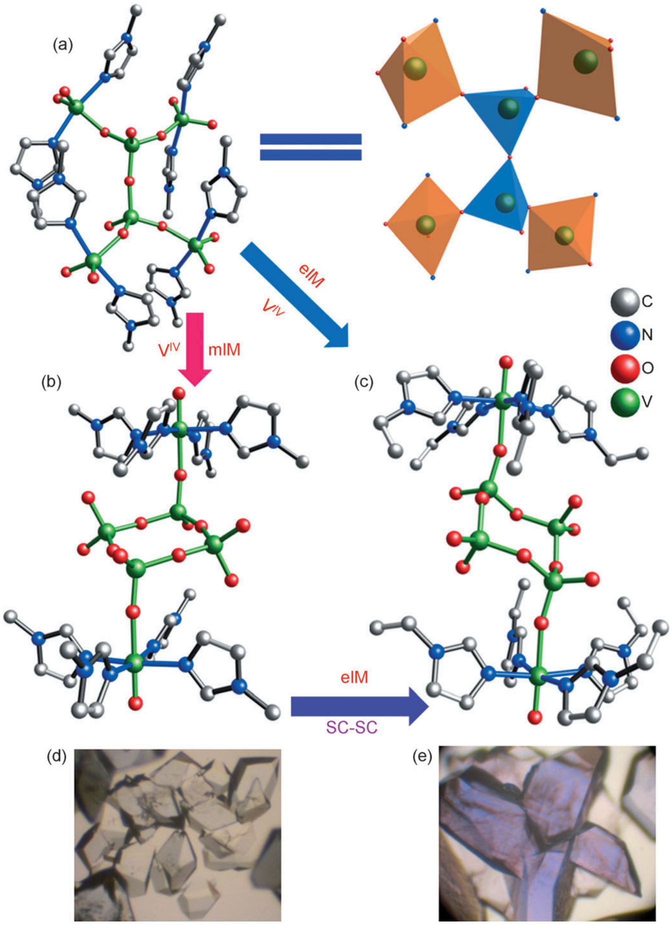


Figure 1. a)–c) Molecular structure of compounds **1**–**3** and the phase transformations among **1**–**3**; d) and e) Optical micrographs of **2** and **3**. Ball and stick: gray C, blue N, green V, red O. SC–SC: single-crystal-to-single-crystal transformation.

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[a] B. Chen,[+] X. Huang,[+] Prof. Dr. B. Wang, Z. Lin, J. Hu, Y. Chi,
Prof. Dr. C. Hu
Key Laboratory of Cluster Science
Ministry of Education of China
School of Chemistry, Beijing Institute of Technology
Beijing 100081 (P.R. China)
Fax: (+86) 10-68912631
E-mail: bowang@bit.edu.cn
cwhu@bit.edu.cn

[b] X. Huang[+]
Shandong Provincial Key Laboratory
of Chemical Energy Storage and Novel Cell Technology
School of Chemistry and Chemical Engineering
Liaocheng University, Liaocheng 252059 (P.R. China)

[+] These authors contributed equally to this work.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201203854.

Given the fact that the presence of V^{IV}/V^{V} can potentially facilitate electron transfer and consequently expedite catalytic reactions,[13] low valent vanadium, V^{IV}, $VO(acac)_2$ was used in reacting with compound **1.** And compounds **2** and **3** were thus obtained with fan-like structures in 1-mIM and 1-eIM, respectively (Figure 1). Compounds **2** and **3** can also be synthesized from NH_4VO_3 and $VO(acac)_2$ in corresponding imidazoles at 100 °C for 3 days. BVS calculations show the oxidation states of all V atoms in compounds **2** and **3** are mixed-valence V^{IV}/V^{V} (four out of the six vanadium atoms are V^{V} and the other two are V^{IV}), which also can be further confirmed by the ESR (the Supporting Information, Figure S1). Specifically, the structure of **2** consists of a mixed-valence V_6 ($V^{IV}{}_2V^{V}{}_4$) cluster with a central $[V_4O_{12}]^{4-}$unit attached on opposite sides of two octahedral $[VO_2N_4]$ groups (Figure 1b). The $[V_4O_{12}]^{4-}$cluster has a cyclic eight-membered $[V_4O_4]$ ring formed by corner sharing of four distorted $[VO_4]$ tetrahedra. Each $[VO_2N_4]$ group adopts a "4+1+1" geometry formed by four N atoms from 1-mIM, one bridging oxygen O_b and one terminal oxygen O_t. Interestingly, the $[V_4O_{12}]^{4-}$clusters within compounds **2** and **3** are different. The eight-membered ring in **2** is nearly coplanar, but the one in **3** is chair-like (Figure 2a and 2b).

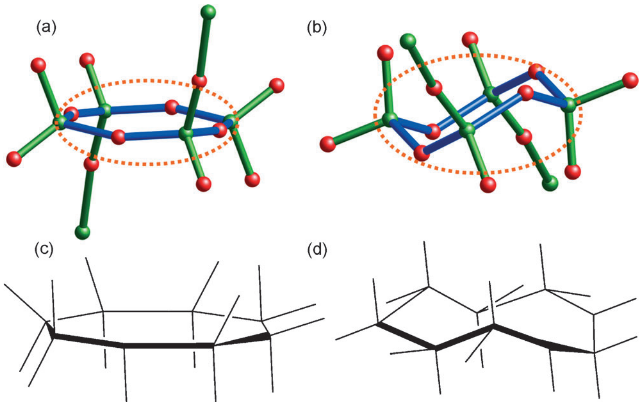


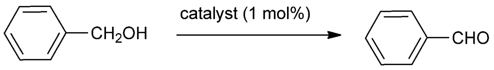
Figure 2. a),b) The structures of $[V_4O_{12}]^{4-}$in **2** and **3**; c) and d) The possible two conformers of cyclooctane.

The geometries of two $[V_4O_{12}]^{4-}$clusters can be viewed as two different conformer products of cyclooctane (Figure 2c and 2d). From a topology perspective, compounds **2** and **3** are very similar to $V_4O_{10}(\mu_2\text{-}O)_2[VO(H\text{-}Ciprof)_2)]_2\cdot 13H_2O$ [Ciprof = 1-cyclopropyl-6-fluoro-1,4-dihy-dro-4-oxo-7-(1-piperazinyl)-quinolone-3-carboxylic acid].[14] However, the POV skeletons in compounds **2** and **3** are functionalized by nitrogen atoms from neutral ligands.

One interesting feature of **2** is that when the crystals were heated to 100 °C in 1-eIM solvent, the light-purple crystals turned purple gradually, which ultimately gave compound **3** within 24 h (Figure 1b–1e) as the eight 1-mIM ligands were replaced by eight 1-eIMs. This single-crystal-to-single-crystal (SC–SC) transformation was further confirmed by single-crystal XRD analyses and the powder XRD patterns of compounds **2** and **3**. This unique SC–SC structural transformation resulting from organic-ligand replacement is rather rare in POM chemistry and indeed has not been observed in any known POV structures.[15]

The oxidative dehydrogenation (ODH) of alcohols is currently a matter of intense research, especially as the resulting aldehydes are critical bulk chemicals in industry. Specifically, the selective oxidation of benzyl alcohol to benzaldehyde is a practically important reaction for the production of chlorine-free benzaldehydes required in the perfumery and pharmaceutical industries, and consequently the catalysts involved have received extensive attention.[16]

Using molecular O_2 as an oxidant offers significant environmental and economic benefits over traditional stoichiometric oxidants. Our initial aerobic-oxidation studies focused on the case of benzyl alcohol (Scheme 1), with an aim to understand the catalytic property of the organic-functionalized POV clusters for developing a new oxidation system in organic chemistry. The reactions were performed in a 50 mL stainless-steel autoclave in the presence of a solvent under O_2 pressure (Scheme 1).



Scheme 1. Aerobic oxidation of benzyl alcohol. Reaction conditions: benzyl alcohol, (1 mmol), catalyst (1 mol %) as to benzyl alcohol, solvent, acetonitrile (5 mL), 130 °C, O_2 (0.2 MPa), 12 h.

To investigate the effectiveness of the organic functionalized POVs (compounds **1** and **3**) relative to that of other vanadium-based catalysts in benzyl alcohol oxidation, the reactions were performed under the same conditions by using V_2O_5, $VOSO_4$ and $VO(acac)_2$ (with and without 1-ethylimidazole present in the reaction media). The conversion and selectivity of each reaction are summarized and illustrated in Figure 3. With regard to the on-going interest in catalytic alcohol oxidation vanadium-substituted POMs, especially

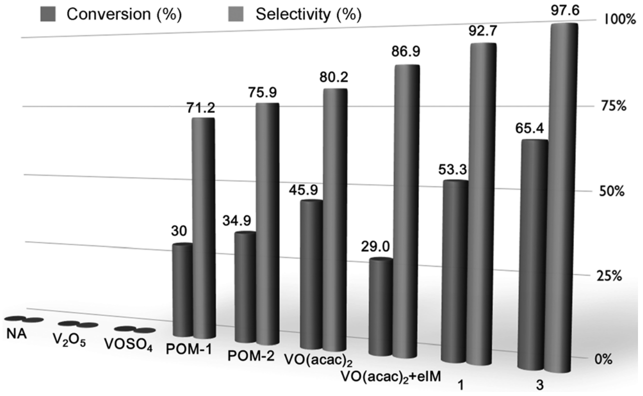
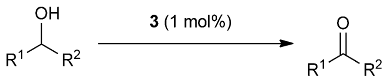


Figure 3. Conversion and selectivity of benzyl alcohol to benzaldehyde with different catalysts. Reaction conditions: benzyl alcohol (1 mmol), catalyst (0.01 mmol), 130 °C, CH_3CN (5 mL), O_2 (0.2 MPa), 12 h, POM-1 = $H_4PMo_{11}VO_{40}$, POM-2 = $H_5PMo_{10}V_2O_{40}$

vanadium-substituted phosphomolybdic acids,[17] we also tested the catalytic activity of $H_4PMo_{11}VO_{40}$ (POM-1) and $H_5PMo_{10}V_2O_{40}$ (POM-2) in the same reactions (Figure 3). After the preliminary optimization, we noted that compounds **1** and **3** were active and more selective for the aerobic oxidation of benzyl alcohol than other vanadium catalysts tested (Figure 3). And indeed, compound **3** outperforms some noble-metal-based compounds reported in the literature, with a conversion of 65 % and a selectivity of 98 % with **3** under 2 bar, compared with a conversion of 52 % and a selectivity of 83 % with $[Pd_{13}As_8O_{34}(OH)_6]^{8-}$ under 50 bar.[18]

Following the success of benzyl alcohol oxidation and evaluating the scope and limitations of the current procedure, oxidation reactions with an array of alcohols were examined by using compound **3** (Scheme 2). A compilation of results for the aerobic oxidation of various additional primary, secondary alcohols, aliphatic cycloalcohol and aliphatic alcohol, along with the corresponding aldehydes and ketones is presented in Table 1. It is noteworthy that (without any further optimization) the oxidation of salicylol using compound **3** proceeded smoothly with a conversion of 100 % and the selectivity for aldehyde was 96.7 %. The preliminary results exhibit that these imidazole-functionalized polyoxovanadium clusters can facilitate the aerobic oxidation of alcohols and serve as highly efficient and selective catalysts (Figure 4).

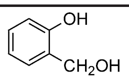
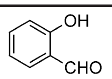
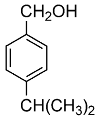
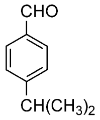
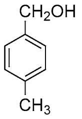
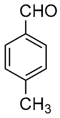
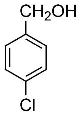
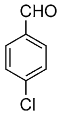
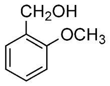
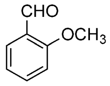
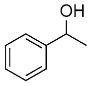
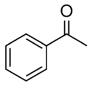
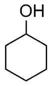
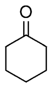


Scheme 2. Scope of aerobic oxidation of alcohols. Reaction conditions: alcohol (1 mmol), catalyst (1 mol %) based on alcohol, acetonitrile (5 mL), 130 °C, O_2 (0.2 MPa), 12 h

Although several oxidation procedures of salicylol are known, in most cases complicated noble-metal-based catalysts, such as Pd[19] and Au,[20] are used. This inevitably makes the oxidation procedure an expensive one. We selected compound **3** as the catalyst for such reactions because it is inexpensive and stable. Compound **3** is also more effective for the aerobic oxidation of salicylol than the above reported noble-metal-based catalysts (the Supporting Information, Figure S11). Furthermore, the isolation of the product and the recovery of the catalyst were easy (see the Supporting Information). The IR spectrum and XRD of the recovered catalyst **3** was identical to that of the freshly prepared catalyst **3** (the Supporting Information, Figures S12 and S13). In addition, the recovered catalyst **3** could be reused for the aerobic oxidation of salicylol in repetitive reactions without an appreciable loss of its high catalytic performance (Conv. of salicylol: 100 % (first run), 99 % (second run), and 99 % (third run), the Supporting Information, Figure S11).

We sought to explore the possible mechanisms of the oxidation of salicylol based on our experiments and also confirm the hypothesis with comparable studies reported previously.[21,22] Specifically we have found that compound **1** can be converted to **2** and **3** upon introducing 1-mIM and 1-eIM, respectively. Compounds **2** and **3** can further undergo a single-crystal-to-single-crystal transformation in which 1-eIM can easily replace 1-mIM and gives single-crystalline **3**. These show that the imidazole ligands can readily leave and re-coordinate to the "outer" vanadium atoms in **1**, **2** and **3**,

Table 1. Results of selective oxidation of alcohols catalyzed by compound **3** using O_2 as the oxidant.[a]

Entry	Alcohols	Product	Conversion [%]	Selectivity [%][b]
1			100	96.7
2			66.0	95.2
3			65.3	98.9
4			65.0	93.1
5			52.8	95.4
6			41.3	92.4
7			12.6	54.0
8	n-$C_7H_{16}CH_2OH$	n-$C_7H_{16}CHO$	10.2	29.0

[a] Reaction conditions: alcohol (1 mmol), compound **3** (0.01 mmol), CH_3CN (5 mL), O_2 (0.2 MPa), 130 °C, 12 h. [b] Selectivity to aldehydes or ketones.

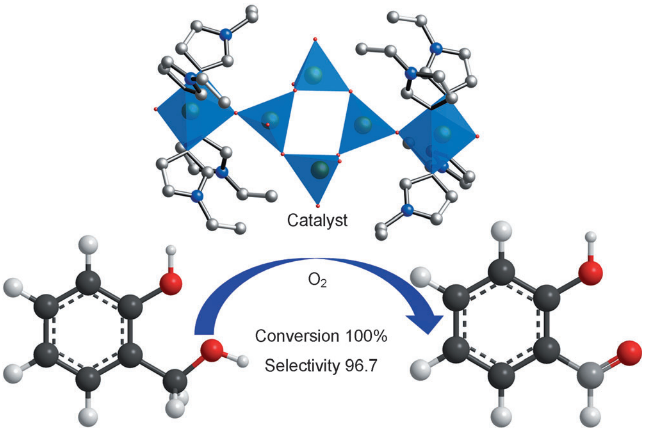


Figure 4. Aerobic oxidation of salicylol under the preliminary optimization of benzyl alcohol.

and consequently generates active vanadium centers for the aerobic oxidation of alcohols.

Based on our results and precedent work, a plausible catalytic mechanism can be proposed and is shown in Figure 5. First, species A reacts with both alcohol and molecular oxygen and consequently strips down two imidazole molecules to form the vanadium(V) species B. Species B further reacts with alcohol and affords a vanadium alcoholate, C. Then, the subsequent dehydration of C by oxidation reproduces a vanadium(IV) species D and the target molecules. Finally, species D reacts with two imidazole molecules to form species A again.

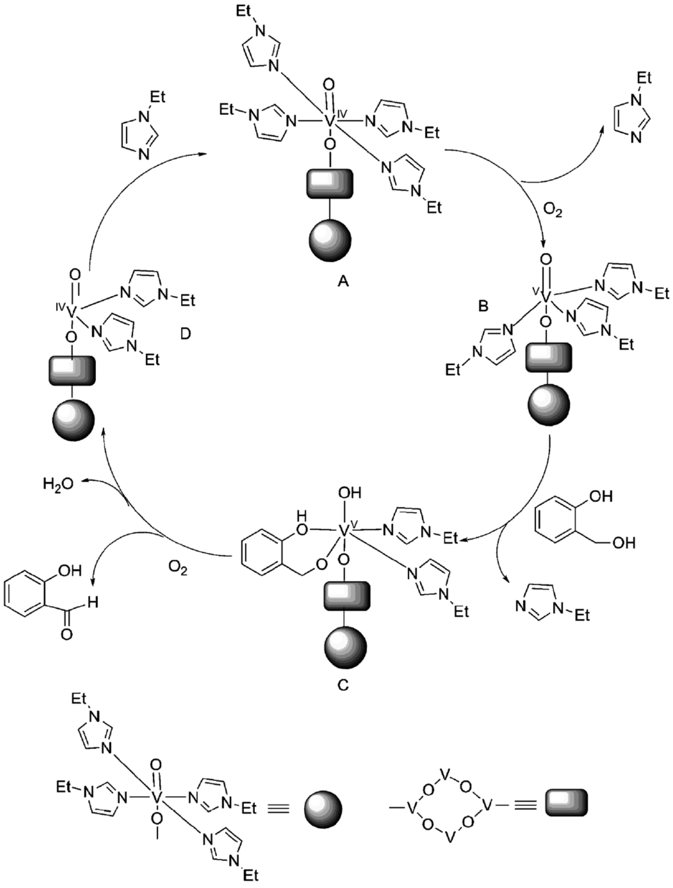


Figure 5. The proposed reaction pathway of oxidation of salicylol.

In summary, we have successfully prepared three new neutral hexanuclear vanadium clusters, named compounds **1**, **2**, and **3**, in imidazoles, in which these versatile organic compounds serve as the coordination ligands, the structural-directing agents, and simultaneously, the reaction media. Compound **1** can be precisely converted to mixed-valent **2** and **3** upon introducing a V^{IV} source in corresponding imidazoles, whereas **2** can undergo single-crystal-to-single-crystal transformation to **3**. These materials are chemically and structurally stable, yet have the long-sought-after characteristic as highly efficient and selective oxidation catalysts of benzyl alcohols by using molecular oxygen as the oxidant. Specifically, under un-optimized conditions, compound **3** exhibits extraordinary efficiency in converting salicylol to salicylaldehyde with high conversion and selectivity (conv. = 100 %, sele. = 96.7 %). Importantly these new vanadium clusters can be easily recycled and reused with unchanged catalytic activity. This opens a new route to functionalize POVs toward catalytic applications and may shed light on discovering more new polynuclear metal clusters. The catalytic cycle and mechanism on such polynuclear mixed-valent vanadium clusters are rather complicated. Indeed, the investigation on other new organo-POV structures by using this approach and the study of the detailed catalytic mechanism are in process, which will be reported in due course.

Experimental Section

Synthesis of 1: NH_4VO_3 (0.234 g, 2 mmol) in 1-methylimidazole (10 mL) was sealed in a 50 mL Teflon-lined stainless steel container, which was heated to 90 °C under autogenously pressure for 72 h. Yield: 50 % (based on V); IR (KBr): $\tilde{\nu}$ = 3136 (m), 1531 (m), 1513(s), 1420 (s), 1277(m), 1228(m), 1098(s), 924 (s), 862(m), 788(s), 726(s), 652(s), 608(m), 490(m) cm^{-1}; elemental analysis calcd (%) for $C_{32}H_{48}N_{16}O_{15}V_6$: C, 31.98; H, 4.02, N, 18.64 (18.34); found: C 31.71; H, 4.61; N, 18.34.

Synthesis of 2: NH_4VO_3 (0.234 g, 2 mmol) and $[VO(acac)_2]$ (0.265 g, 1 mmol) in 1-methaimidazole (10 mL) was sealed in a 50 mL Teflon-lined stainless-steel container, which was heated to 100 °C under autogenously pressure for 72 h. Yield: 81 % (based on V); IR (KBr): $\tilde{\nu}$ = 3125 (m), 1534 (m), 1519(m), 1421 (m), 1281(m), 1230(m), 1095(s), 935(s), 935(s), 890(m), 816(m), 775(s), 662(m), 615(s) cm^{-1}; elemental analysis calcd (%) for $C_{32}H_{48}N_{16}O_{14}V_6$: C 32.41, H 4.08, N 18.89; found: C 31.97, H 4.45, N 18.39;

Synthesis of 3: The synthetic procedure was the same as for compound **2** except that 1-ethylimidazole (10 mL) was used instead of 1-methaimidazole. Yield: 90 % (based on V). IR (KBr): $\tilde{\nu}$ = 3115 (m), 1524 (m), 1446 (m), 1318(m), 1240 (m), 1096(s), 946(m), 925(s), 879(m), 775(m), 750(s), 667(m), 626(w), 527(m) cm^{-1}; elemental analysis calcd (%) for (found) for $C_{40}H_{64}N_{16}O_{14}V_6$: C 37.01, H 4.97, N 17.26; found: 37.38; H 4.89, N 16.91.

X-ray crystallography: The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as CCDC-888578 (**1**), CCDC-888579 (**2**), and 888580 (**3**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was financially supported by the National Natural Science Foundationof China (21231002, 21276026, and 21173021), the 111 Project (B07012), the Program of Cooperation of the Beijing Education Commission (20091739006).

Keywords: alcohols · imidazoles · ligands · oxidation · polyoxometalates · vanadium

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Received: October 29, 2012
Revised: January 10, 2013