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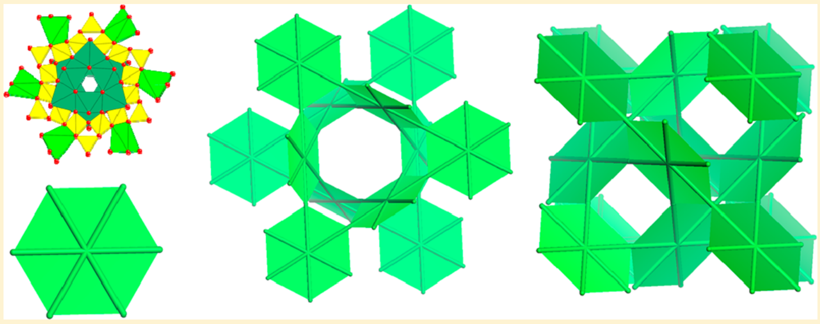
3D Open-Framework Vanadoborate as a Highly Effective Heterogeneous Pre-catalyst for the Oxidation of Alkylbenzenes

Hong Chen,[†,‡] Youqian Deng,[§] Zhengbao Yu,[∥] Huishuang Zhao,[†] Qingxia Yao,[†] Xiaodong Zou,[†] Jan-E. Bäckvall,*[,§] and Junliang Sun*[,†,∥]

[†]Department of Materials and Environmental Chemistry, Stockholm University, SE-106 91 Stockholm, Sweden
[‡]Faculty of Material Science and Chemistry, China University of Geosciences, 430074 Wuhan, China
[§]Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, SE-106 91 Stockholm, Sweden
[∥]College of Chemistry and Molecular Engineering, Peking University, 100871 Beijing, China

Ⓢ *Supporting Information*



ABSTRACT: Three three-dimensional (3D) open-framework vanadoborates, denoted as SUT-6-Zn, SUT-6-Mn, and SUT-6-Ni, were synthesized using diethylenetriamine as a template. SUT-6-Zn, SUT-6-Mn, and SUT-6-Ni are isostructural and built from $(VO)_{12}O_6\ B_{18}O_{36}(OH)_6$ clusters bridged by ZnO_5, MnO_6, and NiO_6 polyhedra, respectively, to form the 3D frameworks. SUT-6 is the first vanadoborate with a 3D framework. The framework follows a semiregular ***hxg*** net topology with a 2-fold interpenetrated diamond-like channel system. The amount of template used in the synthesis played an important role in the dimensionality of the resulting vanadoborate structures. A small amount of diethylenetriamine led to the formation of this first 3D vanadoborate framework, while an increased amount of diethylenetriamine resulted in vanadoborates with zero-dimensional (0D) and one-dimensional (1D) structures. SUT-6-Zn was proved to be an efficient heterogeneous precatalyst for the oxidation of alkylbenzenes.

KEYWORDS: *vanadoborates, open-framework materials,* ***hxg*** *topology, heterogeneous catalysis, oxidation*

■ INTRODUCTION

Inorganic microporous materials such as silicates, borates, phosphates, and germanates attracted great interest during the past decades due to their industry applications in catalysis, adsorption, and separation.[1−5] Group III, IV, and V elements like B, Al, Si, Ge, P are typical elements frequently used in constructing this kind of material. Recently, transition metals, such as zinc, titanium, nickel, etc.,[6,7] were introduced to synthesize new microporous materials for different catalytic applications. Vanadium, one of the most studied elements for catalytic applications, has also been used to synthesize inorganic microporous materials such as vanadogermanates,[8] vanadosilicate,[9,10] and vanadophosphates,[11] which show enhanced catalytic or magnetic properties.[12] As the vanadium compounds show similar bond lengths and coordination environment as germanium, using vanadium to replace those traditional elements for constructing inorganic microporous materials seems very promising. In addition, various types of valence states of vanadium ions (+3, +4, or +5) could also provide interesting catalytic or magnetic properties.

Ever since 1998, when Rijssenbeek reported the first vanadoborate clusters,[13] a great number of vanadoborate clusters such as V_6B_{20} in $[(VO)_6\{B_{10}O_{16}(OH)_6\}_2]^{3-}$,[14] V_6B_{22} in $[V_6B_{22}O_{44}(OH)_{10}]^{8-}$,[15] $V_{10}B_{28}$ in $[Mn_4(C_2O_4)(V_{10}B_{28}O_{74}H_8)]^{10-}$,[16] $V_{12}B_{16}$ in $[(VO)_{12}O_4\{B_8O_{17}(OH)_4\}_2]^{8-}$,[17] $V_{12}B_{17}$ in $[(VO)_{12}O_4\{B_8O_{17}(OH)_4\}\{B_9O_{18}(OH)_4(H_2NCH_2CH_2NH_3)\}]^{8-}$, $V_{12}B_{18}$ in $[(VO)_{12}O_6\{B_3O_6(OH)\}_6]^{10-}$,[13] and $V_{12}B_{32}$[18,19] in $([(VO)_{12}\{B_{16}O_{32}(OH)_4\}_2]^{12-})$ have been reported. Compared with vanadogermanates or vandosilicates, where all cage-like clusters can be derived from the $V_{18}O_{42}$ cluster by replacing n VO_5 square pyramids with n Ge_2O_7 or Si_2O_7 groups (n = 2,3,4),[8] vanadium polyhedra and boron species are much more

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flexible in constructing different types of vanadoborate clusters. Other kinds of transition metals,[16] transition metal complexes,[20,21] or even organic groups[22,21] can be incorporated into the cluster to enhance the diversity of the vanadoborate clusters. For instance, when the $Zn_4(\mu\text{-}B_2O_4H_2)$ group was incorporated into the $V_{10}B_{28}$ cyclic bend, a new type of $Zn_4V_{10}B_{30}$[16] cluster was obtained. Interestingly, while a large number of different types of three-dimensional (3D) vanadogermanate or vanadosilicate frameworks were reported,[8,9] typical vanadoborates only have lots of lower dimensional structures, such as one-dimensional (1D) cluster chain and two-dimensional (2D) net structures. Ian D. Williams[23] et al. claimed 3D microporous vanadoborates a decade ago, but there were no details about the structure. Recently Zhou et al.[24] reported the first dense 3D vanadoborate in which all $V_{12}B_{18}$ clusters are connected by the 3D Na−O−Na network forming a dense structure. However, the Na−O bonds are ionic bonds, and no porosity was observed. Compared with other borates or vanadium-incorporated cluster-based materials where 3D open-frameworks have been widely studied, no 3D open-framework vanadoborate has been reported until now. Here, we synthesized a 3D open-framework vanadoborate, SUT-6 with diethylenetriamines as templates, and Zn, Ni, and Mn polyhedra as linkers. SUT-6-Zn was proved to be an effective heterogeneous oxidation precatalyst.

■ EXPERIMENTAL SECTION

Synthesis. The title compound was synthesized by hydrothermal reaction of $M(NO_3)_2\cdot 6H_2O$ (M = Zn, Ni, or Mn) with diethylenetriamine, $NH_4B_5O_{10}$, NH_4VO_3, and H_3BO_3 in H_2O at 180 °C for 7 days. All chemicals were of analytical grade and used as supplied.

Synthesis of SUT-6-Zn. A mixture of $NH_4B_5O_{10}$ (0.2725 g, 1 mmol), NH_4VO_3 (0.0421 g, 0.4 mmol), H_3BO_3 (0.1212 g, 2 mmol), $Zn(NO_3)_2.6H_2O$ (0.0604 g, 0.2 mmol), $NH(CH_2CH_2NH_2)_2$ (0.11 mL, 1 mmol), and 2 mL of H_2O in a molar ratio of 10:4:20:2:10:110 was sealed in a 5 mL Teflon tube seated in stainless steel, heated at 180 °C for 7 days, and then cooled to room temperature in air. Red-brown octahedral crystals of SUT-6-Zn were recovered by filtration, washed with distilled water, and dried in air, and the yield is about 80% based on NH_4VO_3. The purity was confirmed by powder X-ray diffraction as shown in Figure S1, Supporting Information.

SUT-6-Mn and SUT-6-Ni were synthesized by the same procedure with a recipe similar to that for SUT-6-Zn except for replacing the metal source $Zn(NO_3)_2\cdot 6H_2O$ with $Mn(NO_3)_2\cdot 6H_2O$ and $Ni(NO_3)_2\cdot 6H_2O$.

Structure Characterization. Single crystal X-ray diffraction data were collected at 100 K on an Oxford Diffraction Xcalibur CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å). Data integration and multiscan absorption correction were carried out by the CrysAlis software package[25] from Oxford Diffraction. Structure refinements were done with the SHELXL97 program.[26] Crystallographic data for SUT-6-Zn: cubic, space group $Pn\overline{3}$, a = 18.8164(1)Å, Z = 4, R_1 = 0.0411, and $wR2$ = 0.1404 (all data). Crystallographic data for SUT-6-Ni: cubic, space group $Pn\overline{3}$, a = 18.9393(3)Å, Z = 4, R_1= 0.0675, $wR2$ = 0.1918(all data). Crystallographic data for SUT-6-Mn: cubic, space group $Pn\overline{3}$, a = 18.9341(2) Å, Z = 4, R_1 = 0.0684, $wR2$ = 0.2008 (all data).

Catalytic Reactions. SUT-6-Zn was used as a catalyst to study the oxidation of alkylbenzenes. The typical procedure for oxidation of alkylbenzenes is as follows: SUT-6-Zn (8.4 mg, 0.002 mmol), ethylbenzene (212 mg, 2 mmol), TBHP (1.286 g, 70 wt % in H_2O, 10 mmol), CH_3CN (1 mL), and HOAc (0.2 mL) were stirred at 65 °C for 24 h. The product was identified by ^1H NMR with known literature data. The used SUT-6-Zn was recovered by centrifugation, washed with CH_3CN, and subsequently used in the successive runs. The crude reaction mixture from the catalytical reaction was analyzed by ^1H NMR.

Other Characterizations. The composition of the as-synthesized SUT-6-Zn was determined by CHN elemental analysis and inductively coupled plasma (ICP) analysis. Thermogravimetric (TG) analysis was conducted using a Perkin-Elmer TGA7 on SUT-6-Zn under nitrogen atmosphere in a platinum crucible between 20 and 800 °C at a heating rate of 10 °C min^{-1}. An in-situ PXRD experiment was performed on an X'Pert PANalytical Pro MRD using Cu Kα radiation (λ = 1.5418 Å) and variable divergent slits. The sample was heated in an Anton-Parr XRK900 reaction chamber. The chamber was equilibrated for 2 min prior to each data collection. The samples were heated in air from 30 to 500 °C with a heating rate of 7 °C min^{-1}. PXRD patterns were first recorded at room temperature and 50 °C, then up to 300 °C with an increment of 50 °C, and finally to 500 °C with an increment of 100 °C. Room temperature PXRD used for phase confirmation was also collected on the same diffractometer with a silicon holder. UV−vis-NIR Spectroscopy data were acquired from a single crystal of SUT-6-Zn using a Craic Technologies microspectrometer. The crystal was placed on quartz slides under Krytox oil, and the data were collected from 200 to 1600 nm. The topology of SUT-6 was determined from the TOPOS software package.[27]

■ RESULTS AND DISCUSSION

Crystal Structure of SUT-6-Zn. Single crystal X-ray diffraction analysis revealed that all three compounds are isostructural and crystallize in a cubic space group $Pn\overline{3}$. The representative crystal structure of SUT-6-Zn is discussed in detail here.

The framework of SUT-6-Zn is constructed from $V_{12}B_{18}$ clusters bridged by ZnO_5 polyhedra. The $V_{12}B_{18}$ cluster (Figure 1a) consists of a puckered $B_{18}O_{36}(OH)_6$ ring (Figure 1b) sandwiched by two V_6O_{18} triangles. The $B_{18}O_{36}(OH)_6$ ring contains six $B_3O_7(OH)^{6-}$ units that exhibits a cyclohexane-like chair conformation with the $B_3O_7(OH)^{6-}$ unit at each of the six vertices. According to the fundamental building theory proposed by Kniep Rüdiger,[28] the $B_3O_7(OH)^{6-}$ and $B_{18}O_{36}(OH)_6{}^{24-}$ units can be described as Δ2□:<Δ2□> and 6Δ12□:<12□≥<Δ2□> <Δ2□><Δ2□><Δ2□><Δ2□> <Δ2□>, respectively (□, tetrahedron; Δ, trigonal planar; <··· >, ring motif; [···], branching polyhedron/anion; |, separator for branches; −,=, ≡ ···, 1, 2, 3, ··· common polyhedra). The V_6O_{18} unit is a triangular metal oxo moiety and is composed of six

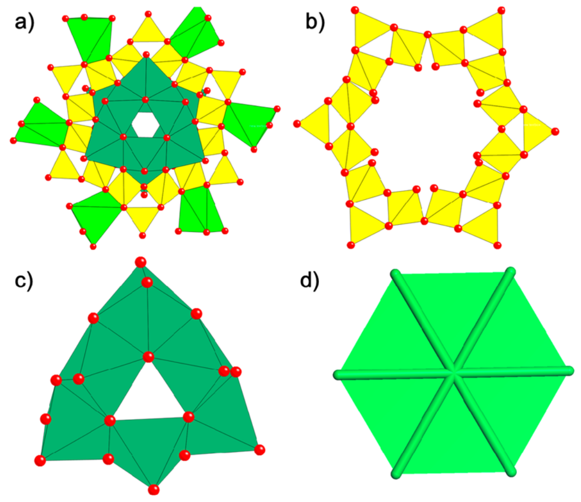


Figure 1. (a) Structure building units in SUT-6-Zn. (b) $B_{18}O_{40}$ ring. (c) V_6O_{19} oxo clusters. (d) Node representation of the $(ZnO_3)_6(VO)_{12}O_6B_{18}O_{36}(OH)_6$ cluster. Color codes: VO_5, dark green; BO_3 and BO_4, yellow; ZnO_5, green; and oxygen atoms, red.

alternatively *cis*/*trans* edge-shared VO_5 square pyramids (Figure 1c). The V_6O_{18} triangles sandwich the puckered $B_{18}O_{36}(OH)_6$ rings through six B-(μ_3-O)-V_2 bonds and three B_2-(μ_3-O)-V bonds with all VO_5 pyramids pointing outside of the cluster. The formed $V_{12}B_{18}$ clusters were then linked into a 3D framework by ZnO_5 polyhedra. Unlike the zinc-incorporated cluster in $\{[Zn(dien)]_2[Zn(dien)(H_2O)]_4[(VO)_{12}O_6[B_{18}O_{36}(OH)_6(H_2O)\}_2 \cdot 15H_2O$,[29] where six zinc atoms show two different coordination configurations with four in octahedra and two in distorted bipyramids, each zinc atom in SUT-6 is coordinated to one water molecule and two pairs of oxygen atoms from two separate $V_{12}B_{18}$ clusters to form a square pyramid.

The 3D framework of SUT-6-Zn can be clearly presented using topology analysis. Each $V_{12}B_{18}$ cluster connects to six $V_{12}B_{18}$ clusters through the ZnO_5 polyhedra in a planar manner (Figure 2a), which can be represented by a hexagon where each ZnO_5 polyhedron is a vertex with the $V_{12}B_{18}$ cluster in the center (Figure 1d). Different from the normal assembling of hexagons where a regular hexagonal layered topology is formed, adjacent hexagons in SUT-6 have a dihedral angle of 70.5° from each other (Figure 2b) and are connected into a cubic network (Figure 2c). This network shows a semiregular ***hxg*** topology,[30] which has the isohedral natural tiling $4^6 \cdot 6^4$ and a transitivity of 1122. Unlike the regular nets which are often found in many open-frameworks especially inorganic structures, the ***hxg*** topology is rare in inorganic structures. Only a few examples were reported in metal−organic frameworks.[31,32] According to our knowledge, SUT-6 is the first example of inorganic frameworks with the ***hxg*** topology.

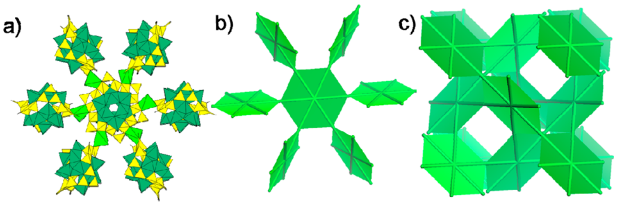


Figure 2. (a) Node (the $V_{12}B_{18}$ cluster) and edge (the ZnO_5 polyhedron) in SUT-6. (b) Orientation of the adjacent hexagons in SUT-6. (c) ***hxg*** topology of SUT-6.

The channel system in SUT-6-Zn is mainly formed by the $V_{12}B_{18}$ clusters with BO_3 and V═O groups pointing to the channel. On the basis of the topology analysis, each edge of the hexagon in Figure 1d contributes two T atoms (B_2O_7), and each connection of the hexagons contributes one T atom (ZnO_5) as shown in Figure 1a. Thus, the channel system in SUT-6 can also be clearly represented by these hexagons. As shown in Figure 3, different windows can be observed along different directions. Along the ⟨100⟩ direction, four edges form 12-ring windows as shown in Figure 3a, but due to the BO_3 and V═O pointing to the channel, this window is almost closed. Along the ⟨110⟩ and ⟨111⟩ directions, 18-ring windows are formed by six edges as shown in Figure 3b−c. Small cage-like voids in SUT-6 are connected through these 18-ring windows and form two interpenetrated diamond-like channel systems as shown in Figure 3d.

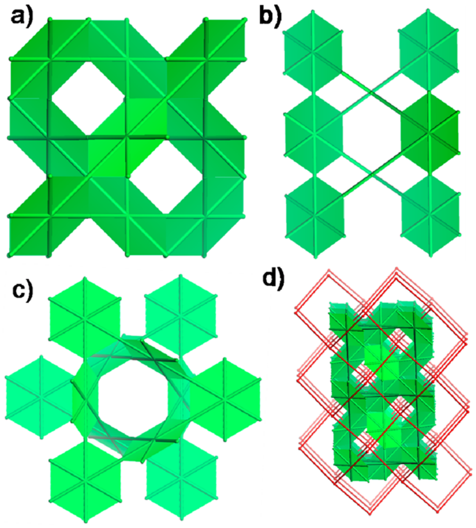


Figure 3. Hexagon representation of SUT-6: (a) 12-ring windows along the ⟨100⟩ direction. (b) 18-ring windows along the ⟨110⟩ direction. (c) 18-ring windows along the ⟨111⟩ direction. (d) Interpenetrated diamond-like channel system is shown as red nets.

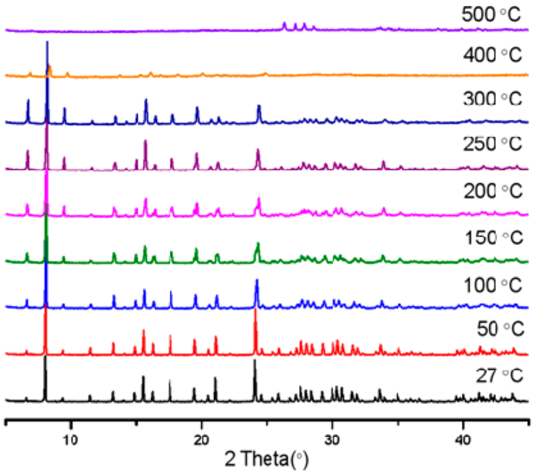


Figure 4. In situ powder X-ray diffraction patterns of SUT-6-Zn in air.

On the basis of the structure refinement and CHN elemental analysis (obsd: weight ratio of C 2.9%; H 2.6%; N 5.8%), the chemical formula of SUT-6-Zn was deduced as $[V_{12}B_{18}Zn_3O_{63}H_{12}] \cdot 3(C_4N_3H_{16}) \cdot 10NH_4 \cdot 5H_2O$ (calcd: C 3.1%; H 2.54%; N 5.75%). The channels are mainly occupied by the organic templates, NH_4^+, and water molecules. Because of the disorders of the guest species, it was not possible to determine their exact positions. TGA (Figure S2, Supporting Information) and in-situ powder X-ray diffraction (Figure 4) show that the guest molecules could be partially removed by heating the sample up to 350 °C while the framework remained intact. By further increasing the temperature, the structure collapsed, and all guest molecules were released slowly.

To check the charge balance of the whole structure, bond valence sum was calculated for vanadium. It shows that vanadium has an average bond valence sum of about +4.094 in SUT-6-Zn without any preferential occupancies for V^{4+} and V^{5+}[13] indicating possible mixed oxidation states of 4+ and 5+. The mixed oxidation explains the red-brown color of the crystals.[33,22] A similar observation was reported in other vanadoborate compounds.[21] This result is inconsistent with the XPS results with a peak at 516.1 eV for V^{4+} and a shoulder at about 517.1 eV for V^{5+}, which are attributed to V^{4+} $2p^{3/2}$ and V^{5+} $2p^{3/2}$, respectively (Figure S3, Supporting Information, ESI).[34] Because of the broad peak width, the accurate ratio of V^{4+} and V^{5+} in SUT-6 could not be obtained from XPS.

SUT-6 could also be obtained using metals other than Zn, for example, Ni and Mn. The structures of SUT-6-Ni and SUT-6-Mn were determined by single crystal X-ray diffraction. Both SUT-6-Ni and SUT-6-Mn have a similar unit cell, the same building units, and the same topology as SUT-6-Zn. The only difference for the three structures is the coordination environments for the metal ions. Unlike the square pyramidal coordination for the Zn ions (Figure 5a), Ni and Mn ions have slightly twisted octahedral coordinations (Figure 5b−c), with four equatorial oxygen atoms from two different BO_4 and two axial oxygen atoms from water molecules.

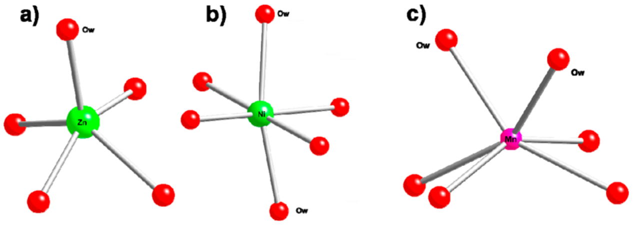


Figure 5. Coordination environment of Zn, Ni, and Mn in SUT-6. Ow indicates the oxygen from water molecule, and the other oxygen atoms are from $V_{12}B_{18}$ clusters.

Synthesis Conditions. It seems that the introduction of metal ions Zn, Ni, or Mn plays a very important role in assembling the open-framework vanadoborate structures since they serve as linkers to connect the isolated $V_{12}B_{18}$ clusters. However, similar synthesis routines were widely used in previous work,[16,17,20,21,24,33,35,36] but no 3D structures were obtained. Zhang et al.[35] and Liu et al.[36]successfully synthesized the zinc complexes and modified the $V_{12}B_{18}$ clusters using ethylenediamine and *N*,*N*′-bis(3-aminopropyl)-1,3-propanediamine, separately. However, the zinc atoms were five-coordinated with one coordination site from a $V_{12}B_{18}$ cluster and the other four sites saturated by either two ethylenediamine ions or one *N*,*N*′-bis(3-aminopropyl)-1,3-propanediamine ion. There is no other coordination site to link the $V_{12}B_{18}$ clusters further. This indicates that the small amount of amines might be the reason for forming 3D vanadoborates in SUT-6.

Therefore, we systematically investigated the synthesis conditions in SUT-6-Zn. We kept all synthesis parameters except for the amount of diethylenetriamine, which was varied from 0.5 to 2 mmol. When the amount of diethylenetriamine was between 0.5 and 1 mmol, pure SUT-6 could be synthesized. When the amount of diethylenetriamine was increased to 1.5 mmol, SUT-6 was formed together with two impurities **VB1** with 1D chains (Figure 6a) and **VB2** with 0D cages (Figure 6b). When the amount of diethylenetriamine was further increased to 2 mmol, a mixture of **VB2** and another 0D cage structure **VB3** (Figure 6c) were obtained without any SUT-6. It is worth noting that although there are Zn ions in the 1D **VB1** structure, the chains are formed by B_2O_5 bridges instead of Zn polyhedra. In fact, the Zn ions are in trigonal bipyramidal coordination, and three of the coordination sites are occupied by diethylenetriamine, which leaves no additional space to link $V_{12}B_{18}$ clusters further. Thus, these results confirm that with high concentration of diethylenetriamine, the possible linker (Zn) is more likely to be saturated by amines and only low dimensional structures were obtained. To synthesize 3D vanadoborates with metal polyhedra as linkers, it is important to use small amounts of amine templates.

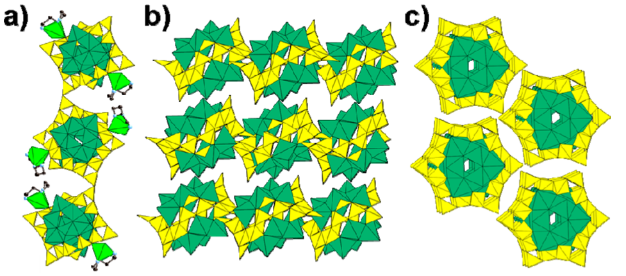


Figure 6. Low-dimensional $V_{12}B_{18}$ structures synthesized with large amounts of amine templates. (a) One-dimensional chain structure with B_2O_5 as bridges in **VB1**; (b) zero-dimensional cage structure in monoclinic symmetry viewed along the *b* axis in **VB2**; (c) zero-dimensional cage structure in trigonal symmetry viewed along the *c* axis in **VB3**.

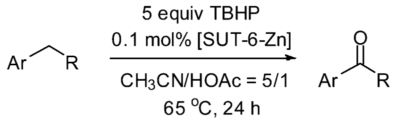
Catalytic Performance. Considering SUT-6-Zn having V-species with mixed oxidation states, which may have potential as a heterogeneous catalyst in benzylic C−H bond oxidation,[37] we were encouraged to investigate its activity in the oxidation of alkylbenzenes to phenylketones. To our delight, the oxidation of ethylbenzene catalyzed by SUT-6-Zn was realized in a mixed solvent of CH_3CN/HOAc (5/1) at 65 °C for 24 h with *tert*-butylhydroperoxide (TBHP) as the oxidant. ^1H NMR analysis of the crude reaction mixture showed that only one product, acetophenone, was formed in a good yield of 75% with 0.1 mol % catalyst loading (Table 1, entry 1). A control experiment omitting SUT-6-Zn under the same conditions gave only <2% yield of product, which confirms that SUT-6-Zn plays an important role as a highly efficient catalyst in this transformation (Table 1, entry 2).

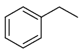
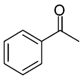
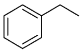
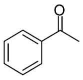
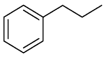
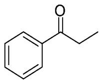
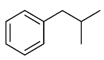
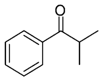
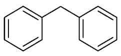
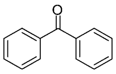
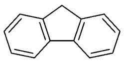
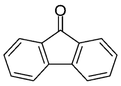
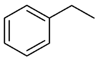
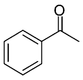
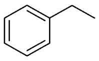
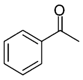
SUT-6-Zn can also catalytically oxidize various alkylbenzenes under the above-mentioned reaction conditions (Table 1, entries 3−6). Structurally similar propylbenzene and isobutylbenzene were tried and gave the corresponding phenylketones in low yields (Table 1, entries 3 and 4). However, SUT-6-Zn could efficiently catalyze the oxidation of diphenylmethane and fluorene to the corresponding ketones in 94% and 91% yields, respectively (Table 1, entries 5 and 6). These results clearly indicate that the oxidations of alkylbenzenes using SUT-6-Zn as the catalyst were not substrate size-selective and that the oxidations most likely occur on the solid surface. The electronic effect of the substrates may also affect the yields to some extent.

The heterogeneous nature of the catalyst was proved by the following control experiment. After the reaction of ethylbenzene, SUT-6-Zn, and TBHP in CH_3CN/HOAc at 65 °C for 2 h, the solid was filtrated off, and the filtrate was subsequently stirred at 65 °C for another 22 h. ^1H NMR analysis of the resulting crude reaction mixture showed that the conversion of ethylbenzene had not changed and was still only 27%, which suggests that this catalyst system is heterogeneous (compare this result with entry 1 in Table 1).

The catalyst can be easily recovered by centrifugation and filtration after the oxidation, and subsequently used in the succesive runs for 8 cycles without significant loss in yield (Figure 7). This remarkable catalytic activity was also demonstrated with a large-scale reaction of ethylbenzene (50 mmol, 5.3 g) catalyzed by only 9 mg of SUT-6-Zn (0.002 mmol) in 72% isolated yield. It should be noted that to the best

Table 1. [SUT-6-Zn]-Catalyzed Oxidation of Alkylbenzenes to Phenylketones[a]



Entry	Substrate	Product	Yield [%][b]
1			77 (75[c])
2[d]			<2
3			38[c]
4			15[c]
5			94[c]
6			91[c]
7[e]			70
8[f]			78

[a] Alkylbenzene (2 mmol), TBHP (5 equiv, 70 wt % in H_2O), SUT-6-Zn (0.002 mmol), CH_3CN (1 mL), and HOAc (0.2 mL) were stirred at 65 °C for 24 h. [b] Yield determined by NMR spectroscopy with anisole as the internal standard. [c] Yield of isolated product. [d] No catalyst. [e] Second cycle. [f] Eighth cycle.

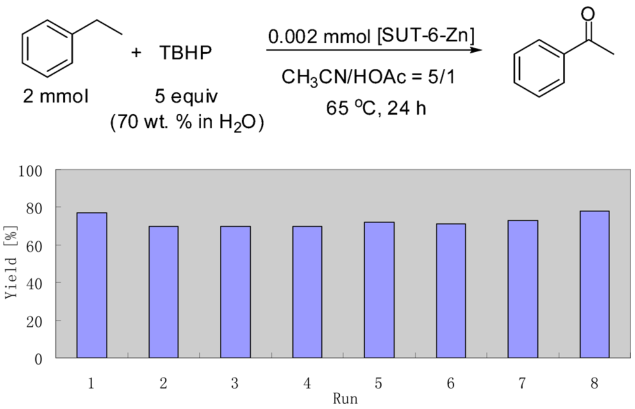


Figure 7. Catalytic oxidation of ethylbenzene by SUT-6-Zn at different runs.

of our knowledge, this catalyst is significantly superior to other reported vanadium heterogeneous catalysts for the oxdiation of ethylbenzene to acetophenone.[37,38]

It has been proposed that benzylic C−H oxidation catalyzed by vanadium-incorporated zinc complexes may involve a C−H abstraction mechanism via a benzylic alcohol intermediate,[37] which was further supported in this case by the successful conversion of 1-phenylethanol to acetophenone catalyzed by SUT-6-Zn in 80% yield (see Supporting Information).

We checked the catalyst recovered after the first and the eighth cycles by powder X-ray diffraction. To our surprise, SUT-6-Zn was converted to a vanadium-incoporated $ZnC_2O_4 \cdot 2H_2O$ during the first reaction cycle, as shown in Figure S6 and S7 (Supporting Information). The crystallinity of $ZnC_2O_4 \cdot 2H_2O$ was improved after each cycle, and the reaction activity remained. In order to find out which is the actual effective catalyst, several control experiments were carried out. We found that a commercial $ZnC_2O_4 \cdot 2H_2O$ did not give any oxidation products, and when NH_4VO_3 or NH_4VO_3 together with $ZnC_2O_4 \cdot 2H_2O$ were used, the reactions afforded acetophenone in yields comparable to those of SUT-6-Zn. However, it was difficult to recycle the catalyst after the oxidation since NH_4VO_3 was soluble in the reaction system in contrast to SUT-6-Zn. These results indicate that the actual heterogeneous catalyst is a vanadium-incoporated $ZnC_2O_4 \cdot 2H_2O$ compound, which is stable and effective throughout the different cycles. The TEM image shows that the recovered catalyst after eight cycles has a plate-like morphology, which is consistent with the different peak widths in the PXRD pattern. ICP results show that the recoved catalyst contains zinc and vanadium with the Zn/V ratio of about 52:1. It was speculated that the active vanadium-incorporated zinc catalyst may be generated in situ in the reaction system. Thus, SUT-6-Zn can be considered as a precatalyst for the oxidation of alkylbenzenes, and the mechanism of the formation of the vanadium-incoporated $ZnC_2O_4 \cdot 2H_2O$ is still under investigation.

■ CONCLUSIONS

In summary, three 3D open-framework vanadoborates (SUT-6-Zn, SUT-6-Mn, and SUT-6-Ni) were synthesized. Single crystal X-ray diffraction revealed that they have the same ***hxg*** topology with 18-ring channel systems. We found that the key experimental factor for achieving 3D vanadoborates was using lower amounts of amine templates to facilitate the transition metal ions to link $V_{12}B_{18}$ clusters into 3D frameworks. The catalytic test shows that SUT-6-Zn works as a precatalyst and has highly effective heterogeneous catalytic oxidation properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

TG, UV−vis-NIR spectrum, simulated PXRD, XPS of SUT-6-Zn, PXRD, TEM image, EDS of SUT-6-Zn after a catalytic reaction, and other details of catalytic reaction performance (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*(J.S.) E-mail: junliang.sun@mmk.su.se.
*(J.-E.B.) E-mail: jeb@organ.su.se.

Notes

The authors declare no competing financial interest.

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