Polydentate 4-Pyridyl-terpyridine Containing Discrete Cobalt Phosphonate and Polymeric Cobalt Phosphate as Catalysts for Alcohol Oxidation

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Dedicated to Prof. Peter Comba on the Occasion of his 65th Birthday

Abstract. Mononuclear discrete cobalt phosphonate $[Co(pytpy)(tBuPO_3H)_2(H_2O)]\cdot H_2O$ (1) and 1D zigzag polymeric cobalt phosphate $[Co(pytpy)_2(dipp)(MeOH)\cdot 2MeOH]_n$ (2) were prepared from the reactions of *tert*-butyl phosphonic acid ($tBuPO_3H_2$) and organic-soluble 2,6-di*iso* propylphenyl phosphate (dippH₂) ligands with $Co(OAc)_2\cdot 4H_2O$ in the presence of 4'-pyridyl 2,2':6',2''-terpyridine in MeOH/CHCl₃(1:1 v/v) solvent mixture at 25 °C. The new compounds

were characterized by analytical, thermo-analytical, and spectroscopic techniques. Further, the molecular structures were established by single-crystal X-ray diffraction studies. Mass spectrometry analysis reveal that both the compounds exist in the solution phase as dimers. Compound **1** was employed as homogeneous catalysts for alcohol oxidation reactions using *tert*-butyl hydroperoxide (TBHP) as the oxidant.

Introduction

Oxidation of alcohols to their corresponding carbonyl compounds is always being appraised as the key functional group transformation reaction in chemical industry.^[1] Conventionally alcohol oxidation is achieved by using stoichiometric amounts of toxic inorganic oxidants such as HNO₃, KMnO₄, and K₂Cr₂O₇, which contribute to excessive toxic byproducts to the ecosystem.^[2] Thus need for non-toxic, atom economic, catalytic and environmentally benign approaches for such reactions were realized in the last few decades.^[3,4] First row transition metal (TM) catalysts are renowned as efficient alcohol oxidation catalysts in the presence of peroxides^[5] or in combination with nitroxyl radicals (e.g., 2,2,6,6-tetramethylpiperidyl-1-oxy TEMPO)^[6] due to their higher natural abundance and inherent ability to exist in more than one oxidation state.^[5d,7] Thus search to achieve best selectivity and efficiency of such alcohol oxidation catalysts is the main impetus for continued research in this field.

2,2':6',2''-Terpyridine (tpy), a tridentate chelating oligopyridine ligand, has been extensively employed for making homo or heteroleptic TM complexes which find potential applications in research areas such as materials science (e.g. photovoltaics and magnetic materials), biomedicinal chemistry (e.g. anti-cancer drugs), and organometallic catalysis.^[8]

Interest in cobalt terpyridine complexes mainly arises due to their ability to act as spin cross over systems.^[9] The one-dimensional cobalt terpyridine complexes such as [Co(pytpy)Cl₂]•MeOH and [Co(pytpy)Cl₂]•2H₂O exhibit a guest dependent 1D spin-crossover phenomenon with thermal hysteresis.^[10] Substitution of 4'-position in pytpy with alkoxyl, hydroxyl or long chain alkyl groups in these complexes imparts interesting phase transition properties apart from the observed spin cross over.^[11]

We have a long standing interest in metallophosphates,^[12] and have extensively reported on discrete and polymeric cobalt phosphates, including clusters of different nuclearity.^[13] Coligands such as bipyridine, phenanthroline and Cl-tpy have also been employed to control their nuclearity.^[13b,13c,14] Cobalt phosphates find potential applications as single source precursors for fine particle ceramics, for CO₂ adsorption, as molecular magnets, and as catalysts for water oxidation reactions.^[12c,13d,15] Although transition metal complexes of tpy, pytpy and their derivatives have been implicated recently to have great potential as catalysts in organic transformation reactions such as asymmetric cyclopropanation of styrenes, alkene hydroboration, etc., they have rarely been employed as alcohol oxidation catalysts.^[8e,16] To the best of our knowledge only few examples of terpyridine containing transition metal complexes were investigated as catalysts for alcohol oxidation reactions.[17]

In a series of recent investigations, we have employed a number of transition metal catalysts for selective and efficient oxidation of alcohols. The catalytic systems that have been studied include, silica supported Schiff base complexes,^[18] dinuclear Mn^{II}, Co^{II} Ni^{II} arylphosphates incorporating 4'-chloro-2,2':6',2''-terpyridine (Cl-tpy) ancillary ligand,^[14] bulky 2,6-dibenzhydryl-4-methylaniline derived Schiff base complexes of Pd^{II}, Cu^{II}, and Co^{II},^[19] and arylimido hexamolybdates.^[20] Continuing on our earlier efforts, in this article we wish to report new cobalt terpyridine complexes containing lipophilic phosphate/phosphonate ligands as homogeneous catalysts for alcohol oxidation reactions.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/zaac.201800091 or from the author.

Results and Discussion

Synthesis and Characterization of 1 and 2

Reacting equimolar quantities of [Co(OAc)₂.4H₂O], tBuPO₃H₂ and 4'-pyridyl-2,2':6',2''-terpyridine (pytpy) in methanol / chloroform solvent mixture (1:1 v/v) at 25 °C leads to the formation of monomeric cobalt phosphonate $[Co(pytpy)(tBuPO_3H)_2(H_2O)]$ ·H₂O (1), whereas reaction of 2,6-diisopropylphenyl phosphate (dippH₂) under similar reaction conditions leads to the formation of polymeric cobalt phosphate $[Co(pytpy)_2(dipp)(MeOH) \cdot 2MeOH]_n$ (2) (Scheme 1). Due to the bulkiness of 2,6-diisopropylphenyl group of dippH₂, only one dippH₂ is coordinated to the central metal atom. This permits the coordination of terminal nitrogen of pytpy (4'-pyridyl) to the central metal atom, which in turn leads to the formation of polymeric complex 2. This phenomenon is not observed when tBuPO3H2 was used because two molecules of tBuPO₃H₂ are coordinated to the central metal atom leaving no space for the coordination of terminal nitrogen of pytpy. The crystalline products of 1 and 2 obtained in these reactions were characterized by different analytical and spectroscopic methods.

Surprisingly, the two phosphorus-based diprotic acids $tBuPO_3H_2$ and dippH₂ give rise to two different product types (viz. discrete monomeric complex 1 and a 1D zigzag polymer 2). ESI-MS of the reaction mixtures suggest that the two different products have gone through a similar dinuclear interme-

diate (Scheme 1 and Figure 1). The ESI-MS spectrum of reactions leading to products 1 and 2 exhibit peaks at m/z 1011 and 1251, whose isotopic pattern exactly matches with the ex-



Figure 1. Section of experimental and simulated ESI-MS spectra of the reaction mixture leading to formation of 1 (a) and 2 (b).



Scheme 1. Synthesis of compounds 1 and 2.

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pected pattern for the dimeric intermediates depicted in Scheme 1. Similarly, the ESI-MS analysis of the isolated single crystals of **1** in solution yields once again the spectra depicted in Figure 1. These results clearly indicate that the dinuclear species is present in the solution for both the compounds, whereas in the solid-state (see below) they assume either a mononuclear or polymeric structure depending on the organic (*tert*-butyl or bulky aryloxy) substituent on the phosphorus.

The FT-IR spectra of 1 and 2 recorded as KBr diluted discs exhibit broad absorptions bands centered around 3400 cm⁻¹ due to the coordinated and lattice water molecules in 1 and methanol molecules in 2. The weak absorptions appearing around 3056, 2968 cm⁻¹ in 1 and 3060, 2967 cm⁻¹ in 2, corresponds to C-H stretching vibrations of pytpy and phosphonate/ phosphate ligands. The absence of any absorption band at around 2350 cm^{-1} in **2** indicates complete neutralization of all P-OH groups on aryl phosphate (dippH₂), whereas in case of 1, the broad absorption band centered around 2364 cm⁻¹ implies the presence of residual P-OH group on tBuPO₃H₂ ligand. The absorption bands appearing at 1147, 1105, and 1053 cm⁻¹ in **1** and 1187, 1093, and 992 cm⁻¹ in **2**, arise due to the O-P-O stretching vibrations and M-O-P asymmetric and symmetric stretching vibrations, respectively (Figure S1, Supporting Information).

Crystal Structures of 1 and 2

Red X-ray diffraction quality single crystals of **1** and **2** were directly obtained from the reaction mixture by slow evaporation of solvent (MeOH/CHCl₃ 1:1 v/v) at room temperature over two weeks. Discrete cobalt phosphonate **1** crystallizes in the triclinic space group $P\bar{1}$, whereas 1D polymeric cobalt phosphate **2** crystallizes in the monoclinic $P2_1/n$ space group.

The asymmetric part of the unit cell of **1** contains one pytpy molecule, one di-cationic Co^{II} ion, two mono-deprotonated *t*BuPO₃H₂, and one coordinated aqua ligand besides one lattice water molecule (Figure 2). The arrangement around Co^{II} is distorted octahedral. The CoN₃O₃ octahedron exhibits meridional-isomeric form around the metal (Figure 2).



Figure 2. Molecular structure of 1 (lattice water molecule and hydrogen atoms and are omitted for clarity).

The Co-N bond lengths fall in the expected range, in which the central-Py Co–N2 bond length is shorter [2.058(2) Å] than the lateral-Py Co-N1 [2.153(2) Å] and Co-N3 [2.196(2) Å] bond lengths of the pytpy unit. The bond lengths for 1 are consistent with those typical for high-spin CoII compounds reported earlier.^[21] The Co-O bond lengths varies from 2.011(2) Å (Co-O5) to 2.123(2) Å (Co-O7), which are again comparable with similar literature reported values for cobalt phosphonates.^[22] The *trans* angle between axial coordination sites (O7-Co-O5 177.07°) is slightly smaller than the ideal value for octahedral arrangement (180°). Both the $tBuPO_3H_2$ molecules are mono deprotonated (Harris notation 1.100) [23] with free P-OH groups [further supported by the presence of a broad absorption at around 2300 cm⁻¹(P–OH) in the FT-IR spectrum, vide supra]. Strong hydrogen bonding interactions occur between the hydrogen atoms of the coordinated water molecule (H7A and H7B) and the phosphoryl oxygen atom of the phosphate ligand (O7-H7B···O1 2.662(2) Å, 158.4(5)°] and pendant pyridine nitrogen atom pytpy [O7-H7A···N4 2.549(2) Å, 159.9(2)°]. The free P–OH and phosphoryl oxygen atoms of adjacent tBuPO₃H₂ molecules also show P-OH···O=P complimentary hydrogen bonding with each other [O2-H2A···O1 2.739(2) Å, 169.5(7)°]. This pattern of hydrogen bonding leads to the formation of hydrogen bond aided water dimers as shown in Figure 3.



Figure 3. Water dimer formation via O–H···O inter and intra molecular hydrogen bonding interaction in **1** above ball and stick model and below space filling model (hydrogen atoms except those involved in hydrogen bonding are omitted for clarity).

The asymmetric part of the unit cell of 2 contains one Co^{II} ion, one doubly deprotonated aryl phosphate (dipp), one pytpy ligand, and one coordinated methanol molecule besides two lattice methanol molecules (Figure 4). The Co^{II} ion has a distorted octahedral arrangement with square base of the octahedron occupied by three nitrogen atoms of pytpy (N1-N3) and one oxygen atom of dipp (O2) ligand; the axial coordination sites are provided by oxygen atom (O5) of coordinated methanol and pendant pyridine nitrogen (N4) of another pytpy ligand. The Co-N bond lengths varies from 2.079(4) to 2.163(4) Å [av. 2.136(4) Å], whereas the Co–O distances vary from 1.957(3) to 2.224(3) Å [av. 2.090(3) Å]. The Co-N bond metrics are comparable with those reported for high spin CoII complexes.^[21] The pendant pyridine and the terpy units are not coplanar but are tilted by a dihedral angle of 37.16°. The aryl phosphate ligand is doubly deprotonated and coordinates to Co^{II} ion through O2 (Harris notation 1.100).^[23] Coordination of chelating terpy unit of one pytpy molecule and pendant pyridine moiety of another pytpy molecule results in the formation of 1D zigzag polymer (Figure 5).

Figure 4. Asymmetric unit of 2 (hydrogen atoms, isopropyl groups on phosphate, and two lattice methanol molecules are omitted for clarity).

Catalytic Studies

The soluble phosphonate 1 was further investigated as alcohol oxidation catalysts for diverse substrates. The initial optimization was performed by using benzyl alcohol as substrate and discrete mononuclear cobalt phosphonate 1 as catalyst. We have used three different catalytic doses (0.25, 0.5, and 1 mol%) in separate catalytic runs to find out the optimum catalytic dose in presence of TBHP as oxidant (see Supporting Information). We have obtained better results with 0.5 mol % of the catalyst (67 % conversion with 94 % benzaldehyde selectivity). Meanwhile we have run catalytic reactions in different solvents, temperatures and time to ascertain the optimum solvent, temperature, and reaction time for higher selectivity and catalytic activity. Solvent optimization studies by employing water, methanol, acetonitrile, hexane, and toluene reveal that the use of acetonitrile as solvent medium results in maximum conversion (67%) with 94% benzaldehyde selectivity (Figure 6). The solvent free reaction shows 64% conversion but with poor selectivity (61 % benzaldehyde). Thus we have chosen acetonitrile as the solvent for further catalytic studies.



Figure 6. Oxidation of benzyl alcohol in different solvents using catalyst **1** [substrate (2.5 mmol), oxidant (1 equiv.) and catalyst (0.5 mol%) at 80 °C for 3 h].



Figure 5. 1D zigzag polymeric view of 2 (hydrogen atoms and isopropyl groups on phosphate are omitted for clarity).

To arrive at the optimum reaction time, aliquots of the reaction mixture were taken at regular intervals of time and subjected to GC-MS analysis. The conversion percentage of benzyl alcohol increases up to 3 h; further continuation of reaction does not produce any noticeable increase in the conversion (Figure 7). Moreover, it should also be noted that running the reaction beyond 3 h also destroys the benzaldehyde selectivity. Therefore it can be concluded that running the alcohol oxidation for 3 h is necessary to obtain maximum conversion and selectivity. Further in order to probe the optimum reaction temperature, the catalysis was carried out at different temperatures and it was observed that 80 $^{\circ}$ C is the optimal temperature for the current catalytic system (Figure 8).



Figure 7. Oxidation of benzyl alcohol at different reaction times using catalyst 1 [substrate (2.5 mmol), oxidant (1 equiv.) and the catalyst (0.5 mol%) at $80 \degree$ C].



Figure 8. Oxidation of benzyl alcohol at different temperatures using catalyst **1** [substrate (2.5 mmol), oxidant (1 equiv.) and catalyst (0.5 mol%) at 80 °C].

By applying the optimized reaction conditions, we have extended the present catalytic study to the different substrates, ranging from aliphatic to aromatic alcohols. As can be seen from Table 1, it is possible to attain 100% selectivity (ketone / aldehyde) for the oxidation of all the substrates excepting 1-pentanol and benzyl alcohol. Owing to the significance of pyridine carboxaldehydes in drug synthesis, we have performed the oxidation of a few pyridine containing alcohols. Though our catalyst yields moderate conversion, here again 100% selectivity (aldehyde) is achieved. Blank experiments (without catalyst or without oxidant) result in no conversion of benzyl alcohol. With the motive to use the polymeric complex **2** as the heterogeneous catalyst, we have carried out the benzyl alcohol oxidation (52% conversion with 78% benzaldehyde selectivity). However, under optimized reaction conditions, polymeric complex **2** completely dissolves in the medium.

Conclusions

Discrete cobalt phosphonate 1 and 1D polymeric cobalt phosphate 2 were isolated by employing pytpy co-ligand in the presence of phosphorus acids tBuPO₃H₂ and dippH₂. The crystal structures of both the compounds were established by single-crystal X-ray diffraction studies. ESI-MS analyses reveal that both the compounds exist as dimers in solution. These compounds were further employed as homogeneous alcohol oxidation catalysts and the optimization studies reveal that our catalysts show better conversion and selectivity in acetonitrile at 80 °C in 3 h. The substrate scope reveals that our catalysts exhibit promising results in the oxidation of pyridine containing alcohols which can lead to the pharmaceutically interesting pyridine carboxaldehye with 100% selectivity. Compounds such as 1 and 2 have a strong potential for exhibiting solvent dependent spin cross over behaviour, which we are currently investigating.

Experimental Section

Material, methods, and instruments: All the reactions were carried out in open atmospheric conditions inside a fumehood, without any special precaution to exclude air and moisture. Melting points were measured in glass capillaries and are reported uncorrected. Infrared spectra were obtained with a Perkin-Elmer Spectrum One FT-IR spectrometer as KBr diluted discs. Microanalyses were performed with a Thermo Finnigan (FLASH EA 1112) microanalyzer. Thermogravimetric analyses were carried out with a Perkin-Elmer Pyris thermal analysis system under a stream of nitrogen gas at the heating rate of 10 K·min⁻¹. The ESI-MS studies were carried out with a Bruker MaXis impact mass spectrometer. Solvents were purified according to standard procedures prior to their use. Commercially available starting materials such as Co(OAc)₂·4H₂O (S.D Fine) were used as procured. 4'-Pyridyl 2,2':6',2''-terpyridine (pytpy),^[24] 2,6-di*iso*propylphenyl phosphate (dippH2)^[25] and tert-butyl phosphonic acid (tBuPO3H2)^[26] were synthesized by following reported literature procedures.

Synthesis of 1 and 2: To a stirred solution of pytpy (61 mg, 0.2 mmol) and phosphate ligand either $tBuPO_3H_2$ (27 mg, 0.2 mmol) in case of **1**, or dippH₂ (51 mg, 0.2 mmol) in case of **2** in MeOH/CHCl₃ (1:1 v/v) solvent mixture Co(OAc)₂·4H₂O (49 mg, 0.2 mmol) in MeOH was added under constant stirring at room temperature. The red color clear solutions obtained in each case was further stirred for 2 h and filtered and kept for crystallization at room temperature. Red diffraction quality single crystals of **1** and **2** were obtained in one week.

Substrate	Conversion /%	Obtained aldehyde/ketone	Selectivity of obtained aldehyde/ketone /%	TON
ОН	67	O	94	134
ОН	16	O	81	32
ОН	27	o	100	54
OH C	31		100	62
ОН	68	€ <mark>N</mark> o	100	136
OH N	59		100	118
HO	66	O V	100	132
но	52	o N	100	104
П	15		100	30
ОН	37		100	74
но	18	o	67	36
ноон	25	он но	100	50

Table 1. Oxidation of alcohols catalyzed by compound 1 in presence of TBHP^{a)}.

a) Reaction conditions: substrate (2.5 mmol), oxidant (1 equiv.) and the catalyst (0.5 mol%) at 80 °C for 3 h.

$$\label{eq:comparametric} \begin{split} & [\textbf{Co}(\textbf{pytpy})(\textbf{tBuPO_3H})_2(\textbf{H_2O})] \cdot \textbf{H_2O} ~(1): \text{ Yield } 198 \text{ g} ~(56\% \text{ based on} \\ & \textbf{tBuPO_3H_2}) \text{ Mp: } > 250 \ ^{\circ}\text{C}. \ C_{28}\text{H}_{38}\text{N}_4\text{O}_8\text{P}_2\text{Co: found (calcd.): C } 48.93 \\ & (49.49); \text{ H } 5.34 ~(5.64), \text{ N } 8.08(8.25)\%. \text{ FT-IR (KBr) } \tilde{v} = 3400 ~(\text{br}), \\ & 3056 ~(\text{w}), 2968 ~(\text{vs}), 2364 ~(\text{br}), 1147 ~(\text{s}), 1105 ~(\text{s}), 1053 ~(\text{s}), 769 ~(\text{s}) \\ & \text{cm}^{-1}. \text{ ESI-MS: calcd. for } C_{48}\text{H}_{46}\text{N}_8\text{O}_6\text{P}_2\text{Co}_2 ~(\text{dimeric form } \text{Mr} = 1010) ~[\text{M} + \text{H}]; m/z~1011 ~\text{found } m/z~1011. \end{split}$$

 $[Co(pytpy)_2(dipp)(MeOH) \cdot 2MeOH]_n$ (2): Yield 180 mg (52% based on dippH₂) Mp: > 250 °C. C₃₅H₄₃N₄O₇P₁Co: found (calcd.): C 57.82 (58.25); H 6.37 (6.00), N 7.97 (7.76)%. FT-IR (KBr) \tilde{v} = 3400 (br), 3060(w), 2967(vs), 1187(s), 1093(s), 992(s) cm⁻¹. ESI-MS: calcd. for C₆₄H₆₂N₈O₈P₂Co₂ (dimeric form Mr = 1250) [M + H]: *m/z* 1251 found *m/z* 1251.

X-ray Crystallography: Single crystal X-ray diffraction data were collected with a Rigaku Saturn 724+ CCD diffractometer with a Mo- K_{α} radiation source ($\lambda = 0.71075$ Å) at 150 K. Rigaku Crystal Clear-SM Expert software was used for data collection. Data integration and indexing were performed with the CrysAlisPro software suite. WinGX module was used to perform all the calculations.^[27] The structures were solved by direct methods (SIR-92).^[28] The final structure refinement was carried out using full-least-squares methods on F^2 using SHELXL-2014.^[29] All non-hydrogen atoms were refined anisotropi-

cally. The hydrogen atoms were refined isotropically as rigid atoms in their idealized locations. Crystal data and structure refinement details for 1 and 2 are given in Table 2

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1829567 (1) and CCDC-1829568 (2) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http:// www.ccdc.cam.ac.uk).

Oxidation of Alcohols: Oxidation of alcohols was carried out in a two necked round-bottomed flask. Prior to the reaction, the flask was equipped with a magnetic bar followed by the sequential addition of acetonitrile, substrate, catalyst and *tert*-butylhydrogen peroxide (TBHP). The obtained catalytic mixture was stirred at 80 °C and the aliquots were taken out to monitor the progress of reaction using GC-MS, where helium was used as the carrier gas.

Supporting Information (see footnote on the first page of this article): Supporting information contains FT-IR, additional ESI-MS, TGA for compounds **1** and **2**, and packing diagram of **2**.

Table 2. Crystallographic details of compounds 1 and 2.

	1	2
Identification code	GB-654	GB-077
Empirical formula	C28H38CoN4O8P2	C35H43C0N4O7 P
FW	679.49	721.63
<i>T /</i> K	150(2)	150(2)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a /Å	8.8810(7)	11.0802(4)
b /Å	11.7155(8)	17,4009(6)
<i>c</i> /Å	16.5459(9)	20.1537(8)
a /°	75.241(5)	90
β /°	89.714(5)	104.215(4)
γ /°	70.565(6)	90
V/Å ³	1563.85(2)	3766.8(2)
Z	2	4
$D(\text{calcd.}) / \text{mg} \cdot \text{cm}^{-3}$	1.443	1.272
μ /mm ⁻¹	0.705	0.547
Θ range /°	2.655 to 24.999	2.085 to 24.999
No. of reflns. collected	17909	28081
Independent reflns.	5496	6627
GOF	1.054	1.065
$R_1 [I_0 > 2\sigma(I_0)]$	0.0354	0.0716
wR_2 (all data)	0.0937	0.1992

Acknowledgements

R. M. thanks SERB, New Delhi for a J. C. Bose Fellowship research grant (SB/S2/JCB-85/2014). *G.A.B.* thank UGC New Delhi for research fellowship. *R. A.* thanks the Department of Science and Technology (DST), SERB for a National Postdoctoral Fellowship (NPDF/2016/00037).

Keywords: Phosphates; Phosphonates; Alcohol oxidation; Cobalt; Catalysis

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Received: March 14, 2018 Published online:



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Polydentate 4-Pyridyl-terpyridine Containing Discrete Cobalt Phosphonate and Polymeric Cobalt Phosphate as Catalysts for Alcohol Oxidation

