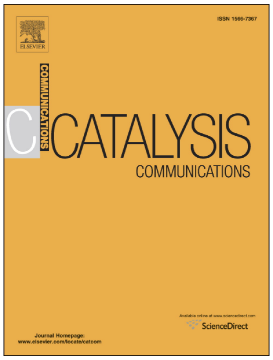

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Self-promoted vanadium-catalyzed oxidation of pyridinemethanol with molecular oxygen

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Abstract

Catalytic oxidation of alcohols containing heteroatoms with molecular oxygen is usually rather challenging, as transition metal catalysts are easily deactivated by heteroatoms. In contrast to conventional results, herein facile oxidation of 2-pyridinemethanol with dioxgyen was observed over simple vanadium catalysts including $VOSO_4$ or $VO(acac)_2$, which seemed much easier than that of benzyl alcohol. 2-Pyridinemethanol could coordinate with the vanadium center, which would promote oxidation of 2-pyridinemethanol itself, rather than deactivate vanadium catalysts. This study would provide a new clue to develop efficient catalysts for transformations of heterocyclic compounds.

Keywords

Catalytic oxidation; vanadium; alcohol; molecular oxygen; heterocyclic; deactivation.

1. Introduction

Heterocyclic compounds of commercial interest, such as pyridine derivatives, find wide applications as intermediates in the chemical and pharmaceutical industries

[1]. Selective oxidation of heterocyclic alcohols is one of the most important routes to obtain aromatic heterocyclic aldehydes [2]. Stoichiometric inorganic oxidants, such as manganese and chromium reagents, are often used both at the laboratory and industrial levels, which deliver considerable amounts of deleterious waste [2,3]. Molecular oxygen is relatively inexpensive and produces water as the only by-product, and the use of oxygen as the terminal oxidant has great benefits from both environmental and economic viewpoints [4]. Thus, researchers have been making extensive efforts to develop efficient catalytic alcohol oxidation with molecular oxygen [5,6].

However, the pyridine ring is more electronegative than the benzene ring, making the two-, four-, and six-ring carbons more electropositive. Oxidation of pyridine analogues generally shows lower activity than that of benzyl alcohols under the same reaction condition. And more importantly, many transition metal catalysts are easily deactivated due to strong coordination/absorption of the nitrogen atom to metal active center, thus oxidation of those alcohols containing heteroatoms is rather a tough problem [7-11]. Only a few reports specifically discussed this issue. For example, Sheldon and co-workers revealed that $[Ru(PPh_3)_3Cl_2]$ was highly efficient for catalytic oxidation of a variety of primary and secondary alcohols into the corresponding aldehydes and ketones. Nevertheless, poor yields were observed during oxidation of some alcohols due to partial coordination of the heteroatoms to the ruthenium center [10]. Gadi Rothenberg *et al* reported that various benzylic and allylic alcohols gave moderate yields over transition-metal oxides supported on nitrogen-doped carbon, meanwhile lower conversion of 2-pyridinemethanol was observed under the same reaction conditions [11]. On the basis of these previous reports, continuous efforts should be made to explore catalytic oxidation of alcohols containing heteroatoms with dioxygen under mild reaction conditions.

In transition metal catalyzed reactions in liquid-phase, solvent molecules, ligands, and substrates usually compete for the metal active coordination sites. Various transitional metal complexes with effective ligands have been broadly investigated by researchers for decades, however, we wonder whether the positive effect of nitrogen atom exists for transition metal-catalyzed alcohol oxidation, rather than the generally discussed metal deactivation. Vanadium has a wide variety of chemistry, and oxovanadium easily forms complexes with heteroatom (*e.g.* O or N) [12,13]. Many vanadium complexes and heterogeneous vanadium catalysts were reported for efficient catalytic oxidation with peroxide or oxygen [12-21]. Recently, we also described several vanadium-catalyzed oxidation reactions with molecular oxygen. Simple vanadyl compounds exhibited unique activity for alcohol oxidation and C-C bond cleavage under optimized reaction conditions [22-25]. Based on these reports above, herein we performed comparative oxidation of 2-pyridinemethanol and benzyl alcohol, and revealed self-promoted vanadium-catalyzed oxidation of pyridinemethanol with molecular oxygen.

2. Experimental

2.1 Materials and apparatus

2-Pyridinemethanol, 4-pyridinemethanol and benzyl alcohol were purchased from Aladdin Chemical Co. Ltd. 2-Picolinic acid was obtained from Shanghai Macklin Biochemical Co. Ltd. 4-Methylbenzyl alcohol and pyridine was provided by Energy Chemical Co. Ltd. 2-(Methoxymethyl)pyridine was obtained from Ark pharm. Acetonitrile (HPLC grade) was supplied by Tianjin Kermel Chemical Reagent Development Center.$VOSO_4 \cdot xH_2O$ was obtained from Alfa Aesar, and dried at 120 °C for 24 h before used. $VO(acac)_2$ (95%) was provided by Aladdin Chemical Co. Ltd.

Unless otherwise stated, other reagents were analytic grade and used as received.

The UV-Vis spectra were recorded on an Agilent Cary 60 spectrometer (USA) with quartz cells at 25 °C, and the wavelength range was 190-800 nm. On-line ATR-IR spectra were recorded on the Mettler Toledo React IR15 spectrometer (Switzerland) with a MCT detector and a diamond probe. The DiComp (diamond) probe was connected via AgX 9.5 mm×1.5 m fiber (silver halide). Data manipulation was carried out with iC IRTM (v. 4.2.26) software. For more experimental details, see supporting information.

2.2 Typical procedure for alcohol oxidation

The catalytic alcohol oxidation was carried out in a stainless autoclave reactor equipped with a magnetic stirring and automatic temperature control apparatus.

The typical procedure for catalytic oxidation: 2-pyridinemethanol (5 mmol, 545.0 mg) and $VOSO_4$ (5 mol%, 43 mg) were put into the autoclave followed by acetonitrile (4 mL). After the autoclave was sealed, dioxygen (0.2 MPa) was charged. Then the autoclave was heated to 80 ^oC within 20 min. After 4 h, the reactor was cooled down to room temperature, and depressurized carefully. Whereafter, a sample of the reaction mixture was taken for GC analysis.

2.3 Products analysis

GC analysis was performed on GC SP-6890 equipped with SE-54 capillary column (30 m×0.32 mm×0.50 μm) and a flame ionization detector. Conversion and selectivity were determined based on area normalization without any purification. Identification of main products was based on GC-MS and the comparison with authentic samples. GC-MS was performed on a Thermo Fisher Trace 1300GC-ISQ_LT with electron ionization (EI) mass spectrometry.

3. Results and discussion

3.1 Oxidation of pyridinemethanols and benzyl alcohols.

Table 1. Catalytic alcohol oxidation with molecular oxygen[a].

Entry	Substrate	catalyst	Conv.[%]	Select.[%][b]
1	Benzyl alcohol	-	N.D	
2	2-Pyridinemethanol	-	N.D	
3	Benzyl alcohol	$VOSO_4$	< 1	-
4	2-Pyridinemethanol	$VOSO_4$	99	99
5	4-Methylbenzyl alcohol	$VOSO_4$	< 1	-
6	4-Pyridinemethanol	$VOSO_4$	77	98
7	Benzyl alcohol	$VO(acac)_2$	33	82
8	2-Pyridinemethanol	$VO(acac)_2$	99	99
9	4-Methylbenzyl alcohol	$VO(acac)_2$	40	84
10	4-Pyridinemethanol	$VO(acac)_2$	70	95
11[c]	Benzyl alcohol	$VOSO_4$	13	86
	2-Pyridinemethanol		99	96

[a] Reaction conditions: 5 mmol substrate, 5 mol% catalyst, 4 mL acetonitrile, 0.2 MPa O_2, 80 ^{o}C , 4 h. [b] Selectivity for the corresponding aldehyde. [c] 2.5 mmol benzyl alcohol and 2.5 mmol 2-pyridinemethanol.

Catalytic alcohol oxidation with dioxygen was performed in liquid phase. No oxidation of benzyl alcohol or 2-pyridinemethanol was observed without a catalyst at 80 ^{o}C within 4 h (Table 1, entries 1 and 2). Less than 1% of benzyl alcohol was converted when $VOSO_4$ was used as a catalyst (Table 1, entry 3), which is consistent with our previous report [22]. Unexpectedly, when 2-pyridinemethanol was subjected to oxidation, 99% conversion was facilely obtained under the same reaction conditions (Table 1, entry 4). The α-C-H bond dissociation enthalpy (BDE) of

2-pyridinemethanol is higher than that of benzyl alchohols (The α-C-H BDEs of 2-pyridinemethanol and benzyl alcohol are approximately 443 and 432 KJ/mol respectively). Generally, pyridinemethanols were much more difficult to be oxidized than benzylic alcohols using transition metal catalysts, or much harsher reaction conditions are usually needed [7-11, 26]. On the contrary, 2-pyridinemethanol was smoothly oxidized in this work. To further verify the results above, we carried out the oxidation of 4-methylbenzyl alcohol with an electron donating group, and no obvious oxidation was observed either (Table 1, entry 5); meanwhile 77% of the 4-pyridinemethanol was converted under the same reaction conditions (Table 1, entry 6). In order to further confirm the difference of activities, VO(acac)$_2$ was used to replace inorganic VOSO$_4$, and oxidation of pyridinemethanol alcohols and benzyl alcohols were performed. Only 33% and 40% conversions were observed when benzyl alchohol/4-methylbenzyl alcohol was oxidized separately (Table 1, entries 7 and 9). Under the same reaction circumstances, 99% and 70% conversions of 2-pyridinemethanol/4-pyridinemethanol alcohols were obtained respectively (Table 1, entries 8 and 10), which are much higher than those of benzylic alcohols. Additionally, when the pressure of O$_2$ was increased to 0.5 MPa, similar phenomenon was also observed (Table S1). Therefore, pyridinemethanols were easier to be oxidized than benzylic alcohols catalyzed by VOSO$_4$ or VO(acac)$_2$, which is obviously different from previous reports [7-11, 26].

Furthermore, competitive oxidation of 2-pyridinemethanol and benzyl alcohol was carried out. An equimolar mixture of benzyl alcohol and 2-pyridinemethanol was subjected to oxidation in the same reactor (Table 1, entry 11). Nearly 99% conversion of 2-pyridinemethanol could still be obtained within 4 h, meanwhile 13% of benzyl alcohol conversion was oxidized. This result suggests that the presence of

2-pyridinemethanol could promote the oxidation of itself as well as benzyl alcohol. Besides molecular oxygen, hydrogen peroxide was often used as an oxidant for vanadium catalyzed oxidation [13, 19]. Oxidation of pyridinemethanols and benzylic alcohols was performed respectively by using hydrogen peroxide instead of oxygen (Table S2). Under the same reaction conditions, the conversion of 2-pyridinemethanol is more than three times higher than that of benzyl alcohol (Table S2, entries 1 and 2), and the conversion of 4-pyridinemethanol is also two times higher than that of 4-methylbenzyl alcohol. These results suggest that self-promotion effect of 2-pyridinemethanol should not be ignored for catalytic oxidation with both dixoygen and peroxide in liquid phase.

Figure 1. Catalytic oxidation of benzyl alcohol by adding different additives.

3.2 The effect of pyridine ring on alcohol oxidation

We therefore wonder whether the interaction between vanadium species and the nitrogen atom occurred, which could affect the catalytic activity of $VOSO_4$. Control experiments were designed to test the effect of *N*-heterocyclic compounds (Reaction conditions: 5 mmol benzyl alcohol, 5 mol% $VOSO_4$, 5 mol% heterocyclic compounds, 4 mL acetonitrile, 0.5 MPa O_2, 80 ^{o}C , 4 h). Catalytic oxidation of benzyl alcohol with molecular oxygen was carried out by adding 5 mol% N-heterocyclic compounds as an additive (Fig. 1). Pyridine, 2-pyridinemethanol, 2-(methoxymethyl)pyridine, and 2-picolinic acid was investigated respectively under the same reaction conditions. No conversion of benzyl alcohol was observed without an additive. As expected, 30% conversion of benzyl alcohol was obtained in the presence of even 5 mol% 2-pyridinemethanol. When 5 mol% of pyridine was added, 25% of benzyl alcohol was converted, indicating that the presence of pyridine ring could also promote the oxidation of benzyl alcohol. Furthermore, when 2-(methoxymethyl)pyridine was used, 56% benzyl alcohol was oxidized, which showed even higher conversion than those using pyridine or 2-pyridinemethanol. However, when 2-picolinic acid was tested, the conversion of benzyl alcohol remarkably decreased to 9%. Simultaneously, different experimental phenomena were observed. In the presence of 2-pyridinemethanol, the reaction mixture became green gradually, while it was blue when pyridine was added. Therefore, the addition of pyridine derivatives affected the catalytic oxidation of benzyl alcohol significantly, and it was the presence of pyridine rings, rather than the hydroxymethyl group, which was important for vanadium-catalyzed alcohol oxidation.

3.3 UV–vis and on-line ATR-IR investigation

In Pd(OAc)$_2$/pyridine catalytic system [27], Shannon S. Stahl *et al* revealed that pyridine would promote the aerobic oxidation of palladium(0) via coordination. Susan K. Hanson and coworkers reported that pyridine could coordinate to dipicolinate vanadium(V) alkoxide complexes as a base [28]. In this work, we speculated that the pyridine ring of 2-pyridinemethanol could activate the vanadium catalyst through *in situ* coordination to the vanadium center as a ligand, and promote oxidation of the substrate itself.

Figure 2. The interaction of 2-pyridinemethanol and VO(acac)$_2$ investigated by UV–vis spectroscopy.

Figure 3. The interaction of benzyl alcohol and VO(acac)$_2$ investigated by UV–vis spectroscopy.

Then we employed UV–vis spectroscopy to investigate coordination of

2-pyridinemethanol (Fig.2). To obtain noticeable changes, $VO(acac)_2$ with strong absorption spectra was selected as the vanadium source. The peak at *ca*. 261 nm is assigned to a π-π* electronic transition of 2-pyridinemethanol (Fig.2, red line). The $VO(acac)_2$ exhibited a high intensity band centered at *ca*. 300 nm with a shoulder at *ca*. 270 nm (Fig.2, blue line). This peak at *ca*. 300 nm was assigned to intra-ligand transitions originated from β-diketonato ligands, and the absorption at *ca*. 270 nm corresponded to that of free acetylacetone in acetonitrile [29,30]. After 2-pyridinemethanol was stirred with $VO(acac)_2$ in the acetonitrile for 4 h, the UV-vis spectrum was collected. The absorption at 300 nm weakened significantly, while a strong and broad peak appeared at *ca*.272 nm, which is the typical absorption band of free acetylacetone (Fig.2, black line) [29-32]. We believe that coordination of 2-pyridinemethanol with the oxovanadium led to release of free acetylacetone, accompanied by a ligand exchange reaction. Then the interaction of benzyl alcohol and $VO(acac)_2$ was studied. By contrast, the peak at *ca*. 300 nm originated from β-diketonato ligands remained strong, and no significant absorption band associated with free acetylacetone was strengthened (Fig. 3). This observation was quite different from that of 2-pyridinemethanol, which should be related with the different oxidation activity of benzyl alcohol and 2-pyridinemethanol.

On-line attenuated total reflection infrared (ATR-IR) spectroscopy is a powerful approach to study chemical reactions [33]. We further investigated the interaction between 2-pyridinemethanol and $VOSO_4$ by on-line ATR-IR. In order to avoid the disturbance of organic molecules, $VOSO_4$ without ligands was selected as the vanadium source. First, 2-pyridinemethanol was dissolved in acetonitrile, and the absorption bands remained stable (Fig. S1). After the addition of 10 mol% $VOSO_4$, a strong absorption peaks at 1119 cm^{-1} appeared soon (Fig. 4), which could be assigned to free sulphate [22,34,35]. One reasonable interpretation is that coordination of 2-pyridinemethanol led to release of free sulphate. We also studied the interaction of benzyl alcohol and $VOSO_4$ by using on-line ATR-IR spectroscopy (Fig. S2 and S3). As we predicted, no significant bands appeared, which was quite different from that of 2-pyridinemethanol. All these results are in good agreement with UV–vis studies and catalytic activities mentioned above.

Figure 4. Interaction between 2-pyridinemethanol and $VOSO_4$ monitored by online ATR-IR.

Nitrogen heteroatom could easily coordinate to oxovanadium form complexes [12,13]. In previous reports on vanadium-catalyzed oxidation, Georgiy B. Shul'pin *et al* described coordination chemistry of vanadium with pyrazinecarboxylic acid, which was highly efficient for catalytic oxidation of various organic substrates [19]. Susan K. Hanson and coworkers demonstrated pyridine could act as both a ligand and a base with the latter directing a two-electron oxidation pathway [28]. Though many examples for oxidation of pyridinemethanol have been described in previous vanadium-catalyzed reports [16-18], self-promoted oxidation of 2-pyridinemethanol was rarely discussed exclusively. We believe that 2-pyridinemethanol could play double roles as a substrate and a ligand. 2-Pyridinemethanol could coordinate with the vanadium center, and *in situ* activate the vanadium catalyst and then promote the oxidation of 2-pyridinemethanol itself. In this context, the presence of N-heteroatom, which could usually deactivate transition metal catalysts, would activate vanadium catalysis instead. Therefore, benzyl alcohol became more difficult to be oxidized compared with 2-pyridinemethanol under the same reaction conditions.

3. Conclusion

In summary, we disclosed the self-promotion effect during vanadium-catalyzed oxidation of pyridinemethanol with molecular oxygen. Pyridinemethanols exhibited much easier to be oxidized than benzylic alcohols under the same reaction conditions. 2-Pyridinemethanol could play both roles as a substrate and a ligand. The N-heteroatom of 2-pyridinemethanol would *in situ* coordinate to the vanadium center and promote oxidation of 2-pyridinemethanol itself. This study would provide a new clue to develop efficient catalysts for transition-metal catalyzed transformations of heterocyclic compounds.

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CRediT author statement

Yangyang Tang: Investigation, Formal analysis. **Zhongtian Du**: Supervision, Conceptualization, Writing-Original Draft. **Meijin Li**: Investigation, Validation. **Wanhui Wang**: Supervision, Writing-Reviewing and Editing**. Yonghou Xiao**: Resources, Methodology.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary data

Supplementary material

References

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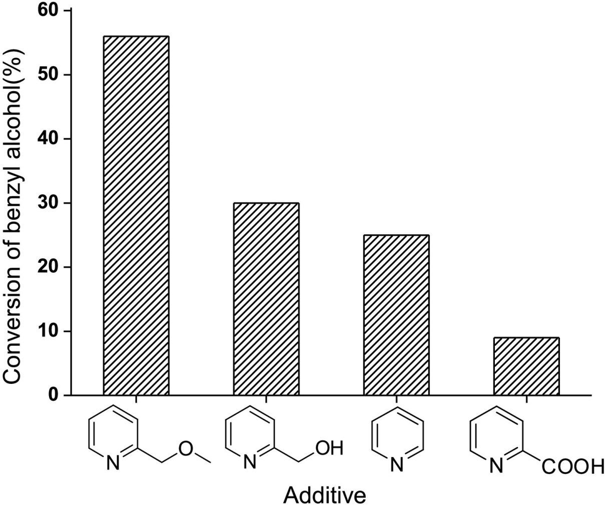
Graphical abstract

Highlights

- Metal catalysts are easily deactivated by heteroatoms due to strong coordination.
- Self-promoted vanadium-catalytic oxidation of 2-pyridinemethanols was observed.
- 2-Pyridinemethanol could play double roles as a substrate and a ligand/base.
- 2-Pyridinemethanol could activate vanadium catalysts, rather than deactivation.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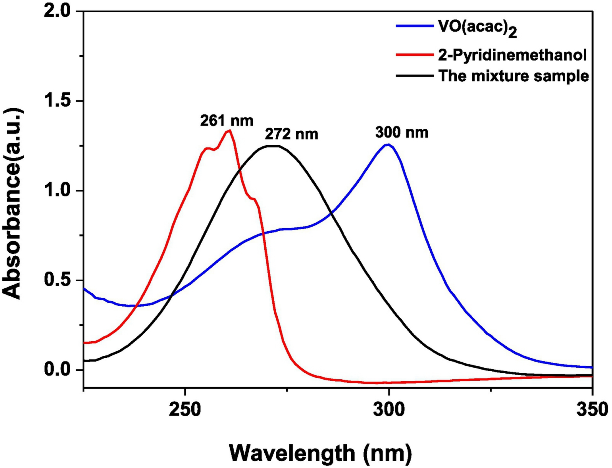
N
N
COOH
Additive

Figure 1



2.0
1.5
1.0
0.5
0.0
Absorbance(a.u.)
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350
Wavelength (nm)
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2-Pyridinemethanol
The mixture sample
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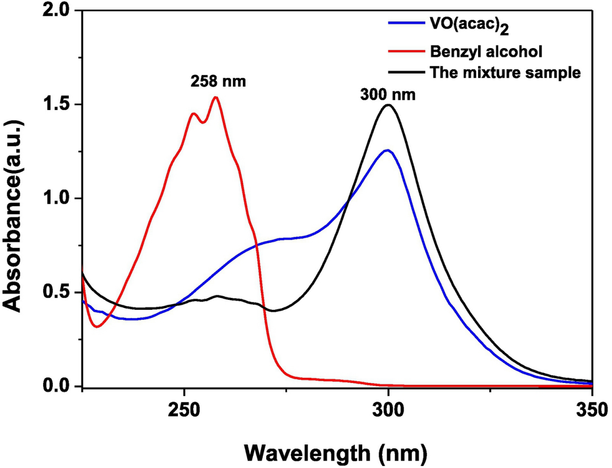
272 nm
300 nm

Figure 2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350
Wavelength (nm)
VO(acac)$_2$
Benzyl alcohol
The mixture sample
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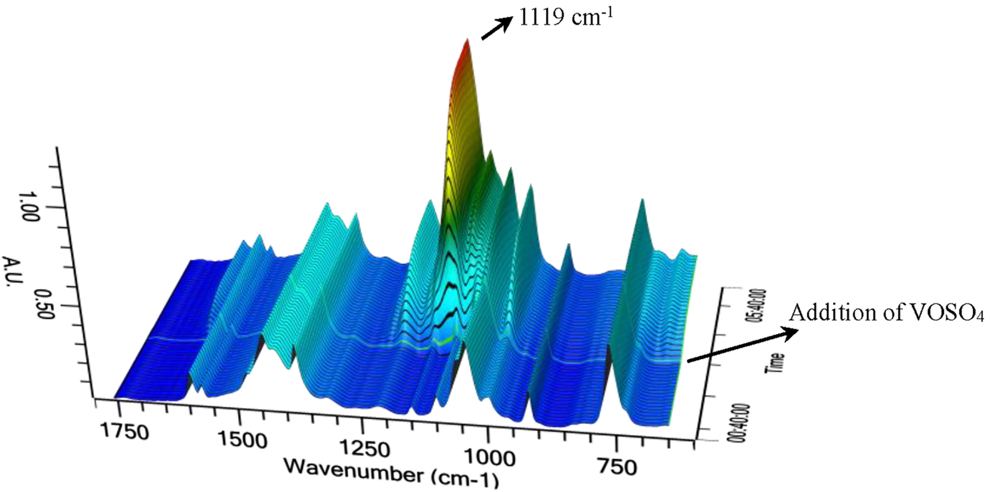
300 nm

Figure 3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Time
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Figure 4