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Vanadium catalyzed direct synthesis of imines from amines or alcohols and amines by an aerobic oxidative reaction under mild conditions

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ABSTRACT

The direct synthesis of imines from amines or alcohols and amines by vanadium catalyzed aerobic oxidation was developed. Without an additive or promoter, various symmetrical and unsymmetrical imines were obtained in good to excellent yields under mild conditions with air as an environmentally benign oxidant. The catalyst is very easy to prepare and use, and this catalytic system is also effective for the synthesis of heteroatom-containing imines.

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Imines are an extremely important class of compounds in chemistry and biology that are used in the synthesis of a wide range of biologically and pharmaceutically active compounds, heterocycles, and natural products [1–3]. Imines containing reactive carbon-nitrogen double bonds are versatile intermediates in many organic reactions such as cyclization, reduction, addition, and condensation [4,5]. The traditional procedure for imine synthesis is the condensation reaction of carbonyl compounds with primary amines. This transformation is usually carried out under acidic conditions, and it is limited by the use of the dehydrating agent or apparatus [6,7]. The required carbonyl compounds are usually obtained from alcohols by oxidation. Therefore, developing new methods for the direct synthesis of imines is still an essential task in current imine chemistry.

In recent years, a range of methods for the preparation of imines have been developed such as one-pot tandem reactions

of alcohols with amines [8–10], self-condensation of primary amines with oxidant [11,12], and oxidation of secondary amines [13,14]. Among these, the dehydrogenative coupling of alcohols with amines under inert oxidant-free conditions has shown high atom efficiency [15–22]. However, in those methods, scarcely available noble metal catalyst complexes or high reaction temperatures are required. A more appealing alternative approach to the synthesis of imines is the direct one-pot oxidative reaction from the greener, cheaper, more readily available and more stable alcohols with amines. Although several reported methods with stoichiometric amounts of reactive oxidant and reagents such as MnO_2 or $\text{Ph}(\text{OAc})_2$ can achieve this transformation, large amounts of undesired wastes are produced [23,24]. From the viewpoint of green and sustainable chemistry, the use of molecular oxygen as the terminal oxidant has advantages, including abundance, low cost, improved safe-

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ty, and benign byproducts. Heterogeneous catalysts such as Pd [25–27], Pt [28], Au [8,9,29–31], Ag [32], and Ru [33] were employed to achieve this transformation. In this process, the catalyst preparation is complex. Moreover, some of the catalysts require pure oxygen as the oxidant and a high reaction temperature to give high yields of products. Very recently, we developed a non-noble metal heterogeneous MnO_x/HAP catalyst for the direct imine formation by the oxidative coupling of alcohols and amines in the absence of an additional base using air as the terminal oxidant [34]. Although recently developed transition metals such as Fe [35], Cu, [36–39], and Pd [40] have been used as catalysts for imine synthesis with molecular oxygen as the terminal oxidant under mild conditions, they need large amounts of ligands, additives, and bases, which make them less attractive for practical purposes. Qiu et al. [41] reported a highly efficient, simple, and versatile transition metal-free aluminum-based metal-organic framework catalytic system for the oxidative coupling of amines to imines.

Vanadium-based catalysts have been widely used in aerobic oxidation reactions [42]. In contrast, vanadium as the catalyst for the aerobic oxidative synthesis of imines is rarely reported. In 2010, Kodama et al. [43] reported the direct synthesis of imines from the oxidation of amines with an oxovanadium complex bearing 3-hydroxypicolinic acid (H_2phic) under an atmosphere of molecular oxygen, but the catalyst system suffered from the drawbacks of a relatively high temperature, poor substrate scope, and low product yield. Recently, Hanson et al. [44,45] discovered that the vanadium complex $(\text{HQ})_2\text{V}^{\text{V}}(\text{O})(\text{O}^i\text{Pr})$ (HQ = 8-quinolinate) could catalyze the oxidation of alcohols to the corresponding carbonyl compounds and C–C bond cleavage of lignin models. Here, we demonstrate that the aerobic oxidative synthesis of imines directly from the oxidative reactions of coupling of primary amines and alcohols with amines can be realized with an easily prepared vanadium complex $(\text{HQ})_2\text{V}^{\text{V}}(\text{O})(\text{O}^i\text{Pr})$ using air as the oxidant. Without any additional additive or promoter, diverse types of substituted imines were obtained in good to excellent yields under mild conditions.

All chemicals used in this study were analytical grade, commercially available and used without further purification unless otherwise noted. $(\text{HQ})_2\text{V}^{\text{V}}(\text{O})(\text{O}^i\text{Pr})$ was synthesized by the literature method [43]. All experiments were carried out in a Teflon-lined 316 L stainless steel autoclave (inner volume 100 ml) equipped with magnetic stirring. GC analysis of yields was performed on an Agilent 7890A with a flame ionization detector (FID). All products were confirmed by GC-MS with an Agilent 7890A GC/5973 MS detector with a SE-54 capillary column, 30 m \times 350 μm \times 0.5 μm . The operating conditions were: FID detector, 300 $^\circ\text{C}$; injection, 250 $^\circ\text{C}$; carrier gas, N_2 (20 ml/min). All substrates and their products, unless otherwise noted, were detected under the conditions: column temperature, 100 $^\circ\text{C}$ for 7 min, raised to 250 $^\circ\text{C}$ at a rate of 15 $^\circ\text{C}/\text{min}$. To provide sufficient detail to enable others to repeat the experiments, methods already published are indicated by a reference, but new and modified experimental procedures are described in detail, and the compositions of the catalysts are given clearly.

For a general procedure for the oxidation of amines to imines, a mixture of catalyst V (21 mg, 0.05 mmol) in CH_3CN (2 ml) was stirred for 1 min at room temperature in a 25-ml flask. Then, benzylamine (107 mg, 1 mmol) was added to the mixture. The resulting mixture was transferred to an autoclave. After the autoclave was sealed, air was charged to 0.1 MPa. The mixture was stirred at 60 $^\circ\text{C}$. After the reaction was completed, the reactor was quickly cooled to room temperature. Excess air was depressurized slowly. GC analysis of the reaction mixtures using biphenyl as an internal standard gave 96% yield of *N*-(benzylidene)benzylamine.

For a general procedure for the oxidation of alcohols and amines to imines, a mixture of catalyst V (21 mg, 0.05 mmol) in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (2 ml) was stirred for 1 min at room temperature in a 25-ml flask. Then, benzyl alcohol (216 mg, 2 mmol) and aniline (93 mg, 1 mmol) were added to the mixture. The resulting mixture was transferred to an autoclave. After the autoclave was sealed, air was charged to 0.1 MPa. The mixture was stirred at 80 $^\circ\text{C}$. After the reaction was completed, the reactor was quickly cooled to room temperature. Excess air was depressurized slowly. GC analysis of the reaction mixtures using biphenyl as an internal standard gave 85% yield of **5a**.

For a general procedure for obtained isolated yield, after reaction, the solvent was concentrated in *vacuo*, and the resultant crude mixture was purified by column chromatography on neutral alumina gel with a mixture of ethyl acetate/petroleum ether/triethylamine as eluent. The alumina gel was preneutralized with 1% (*v/v*) triethylamine in petroleum ether before packing.

Initially, a range of catalysts were applied to the transformation of benzylamine to *N*-(benzylidene)benzylamine in toluene under an atmosphere of air at 60 $^\circ\text{C}$ (Table 1, entries 1–4). Among the catalysts examined, $(\text{HQ})_2\text{V}^{\text{V}}(\text{O})(\text{O}^i\text{Pr})$ was found to be the best catalyst for this transformation with 83% yield. Other vanadium catalysts such as VOSO_4 and V_2O_5 showed lower catalytic activity. The catalyst precursor $\text{VO}(\text{acac})_2$ gave a low yield of the product. The nature of the solvent had a crucial impact on the reaction. Thus, several solvents were screened. CH_3CN as solvent gave the best catalytic activity compared to other solvents such as toluene, $\text{ClCH}_2\text{CH}_2\text{Cl}$, and MeOH (Table 1, entries 6–8). When the temperature was decreased to 40 $^\circ\text{C}$, only 40% yield was obtained, suggesting that an elevated temperature was essential for a high yield of the product (Table 1,

Table 1
Optimization of reaction conditions.

Entry	Catalyst	Solvent	Yield ^a (%)
1	VOSO_4	toluene	1.3
2	V_2O_5	toluene	0.53
3	$\text{VO}(\text{acac})_2$	toluene	2.6
4	$(\text{HQ})_2\text{V}^{\text{V}}(\text{O})(\text{O}^i\text{Pr})$	toluene	83
5 ^b	$(\text{HQ})_2\text{V}^{\text{V}}(\text{O})(\text{O}^i\text{Pr})$	toluene	86
6	$(\text{HQ})_2\text{V}^{\text{V}}(\text{O})(\text{O}^i\text{Pr})$	CH_3CN	96
7	$(\text{HQ})_2\text{V}^{\text{V}}(\text{O})(\text{O}^i\text{Pr})$	$\text{ClCH}_2\text{CH}_2\text{Cl}$	70
8	$(\text{HQ})_2\text{V}^{\text{V}}(\text{O})(\text{O}^i\text{Pr})$	MeOH	27
9 ^c	$(\text{HQ})_2\text{V}^{\text{V}}(\text{O})(\text{O}^i\text{Pr})$	CH_3CN	40

Reaction conditions: benzylamine 1 mmol, catalyst 5 mol%, solvent 2 ml, 0.1 MPa air, 60 $^\circ\text{C}$, 12 h.

^a Determined by GC using internal standard. ^b 80 $^\circ\text{C}$, 6 h. ^c 40 $^\circ\text{C}$, 12 h.

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