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# Environmentally benign synthesis of amides and ureas via catalytic dehydrogenation coupling of volatile alcohols and amines in a Pd-Ag membrane reactor

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## ABSTRACT

In this study, we report the direct synthesis of amides and ureas via the catalytic dehydrogenation of volatile alcohols and amines using the Milstein catalyst in a Pd-Ag/ceramic membrane reactor. A series of amides and ureas, which could not be synthesized in an open system by catalytic dehydrogenation coupling, were obtained in moderate to high yields via catalytic dehydrogenation of volatile alcohols and amines. This process could be monitored by the hydrogen produced. Compared to the traditional method of condensation, this catalytic system avoids the stoichiometric pre-activation or in situ activation of reagents, and is a much cleaner process with high atom economy. This methodology, only possible by employing the Pd-Ag/ceramic membrane reactor, not only provides a new environmentally benign synthetic approach of amides and ureas, but is also a potential method for hydrogen storage.

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## 1. Introduction

Supported Pd-based composite membranes possess many attractive properties such as high and exclusive hydrogen permeability, high thermal stability, moderate chemical resistance and mechanical strength, making them one of the most applicable candidates for the selective removal of hydrogen [1,2]. This offers unique opportunities to achieve dehydrogenative (oxidative) organic transformations which are otherwise impossible under the conventional reaction conditions. For example, we have previously demonstrated an environmentally friendly method of producing ethyl acetate from ethanol in a quantitative conversion and yield using an ultrathin Pd-Ag/ceramic membrane reactor. Since such a reaction can only be carried out at a reaction temperature higher than the boiling point of the reactant (ethanol 78 °C) and therefore, the produced hydrogen needs to be removed from the

reaction system to overcome chemical equilibrium and also to avoid pressure build-up. The selective removal of hydrogen by an ultrathin Pd-Ag membrane reactor was demonstrated to be a viable solution [3]. From the previous studies we also noticed that the reaction rate of dehydrogenative reactions is typically slow, presumably because of the relatively low reaction temperature. Therefore, a relatively long reaction time (typically in several hours) is required in order to achieve high conversion rate, but this also imposes a high requirement in membrane selectivity since otherwise the material loss during the reaction will be substantial. A membrane selectivity over 2000 for H<sub>2</sub>/N<sub>2</sub> was used in our previous studies as a good indicator of membrane quality [3]. Such a high selectivity requirement can be easily achieved by Pd-Ag membranes fabricated through a silver concentration-controlled co-plating method, but it is very challenging for other hydrogen selective membranes, such as polymer, silica, zeolite or carbon molecular sieve membranes [4]. The main disadvantage of the Pd-Ag membrane is its high material cost, but this can be well justified by the high value-added products.

Herein, we report the efficient synthesis of amides via catalytic

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dehydrogenative coupling of volatile alcohols and amines, and ureas using methanol as a non-toxic carbonyl source in an ultrathin Pd-Ag ceramic membrane reactor. The amide linkage is a common and very important functional group which contributes to the special properties of peptides, proteins, beta-lactam antibiotics, and numerous synthetic polymers [5]. Traditional methods of preparing amides mainly involve the use of activated acid derivatives (including acid chlorides and anhydrides). These processes usually require a stoichiometric amount of activating reagents, produce large amounts of chemical waste, and involve tedious procedures for separation [6]. The development of atom economic reactions is an important aspect of green chemistry, which aims in the elimination or minimization of pollution caused by unwanted side-products. The direct synthesis of amides from alcohols with amines by extrusion of hydrogen to construct amide bonds has recently been reported [7–17]. This environmentally friendly approach does not require the use of stoichiometric amounts of oxidants, and hydrogen is produced as an additional value-generating product. The Milstein catalyst, carbonylhydrido [6-(di-*t*-butylphosphino-methylene)-2-(*N,N*-diethyl-aminomethyl) 1,6-dihydropyridine] ruthenium (Fig. 1, complex II), via aromatization-dearomatization of the central pyridine ring, has shown significant catalytic activities towards the direct synthesis of amides from alcohols and amines [7]. In the presence of the Milstein catalyst, a wide range of amides have been obtained through the dehydrogenative acylation of amines with alcohols, with the extension of the application for the synthesis of bis-amides and polyamides. However, high reaction temperatures are normally required in order to achieve good chemical yields. The utilization of these reactions to alcohols and amines with lower boiling points, such as methanol, ethanol and 1-propanol, still remains a challenge.

Urea derivatives are important biologically active compounds, which are frequently used in a variety of areas such as pharmaceuticals, chemical dyes, and agricultural pesticides [18]. These compounds are commonly synthesized using highly toxic phosgene or phosgene derivatives, such as carbodiimidazole (CDI), triphosgene or *S,S*-dimethyl dithiocarbonate (DMDTC) [19]. Amines can also be oxidatively carbonylated with carbon monoxide in the presence of transition metal catalysts [20–24]. However, aside from the toxicity of CO, there exists the risk of explosions due to the usage of high pressures of CO. An alternative route of synthesizing urea derivatives is the direct reaction of amines with carbon dioxide [25,26], but in general this method requires harsh reaction conditions (around 200 °C,  $P_{\text{CO}_2} > 6$  MPa), or the presence of stoichiometric amounts of bases such as  $\text{NEt}_3$ , or DBU [27]. Therefore, it is desirable to develop an environmentally benign and mild reaction for the construction of ureas.

Methanol, the simplest alcohol with an annual output of more than 40 million tons, has found widespread applications [28,29]. It processes a high hydrogen to carbon ratio and carries 12.5 wt% of hydrogen. The production of hydrogen from methanol has received attention due to several advantages as compared to other fuels. For example, methanol is biodegradable and is liquid at atmospheric conditions, which makes it easy to manipulate. In addition, the reforming temperatures is low (200–300 °C) [30],

which is much lower than that of other common fuels such as methane (> 500 °C) and ethanol (ca. 400 °C) [25,31]. For the dehydrogenation of methanol, there is a parallel side-reaction of the decomposition of methanol to CO. At 200 °C the equilibrium constant for the formation of formaldehyde is  $3.4 \times 10^{-2}$ , while the equilibrium constant for the decomposition of methanol to CO is  $2.6 \times 10$  [32]. While the complete dehydrogenation of methanol is favoured at equilibrium, formaldehyde may combine with one molecule of amine to form a formamide, with the liberation of one molecule of  $\text{H}_2$ . The formyl carbonyl will provide another position for the combination of one more amine. This will allow the direct synthesis of ureas from methanol and amines with a suitable catalytic system, utilizing methanol as a carbonyl source.

## 2. Experimental

### 2.1. Materials

Silver nitrate ( $\text{AgNO}_3$ ), palladium chloride ( $\text{PdCl}_2$ ), palladium sulfate ( $\text{PdSO}_4$ ), and ethylene diamine tetra-acetic acid disodium salt dihydrate ( $\text{Na}_2\text{EDTA}$ ), ammonia ( $\text{NH}_4\text{OH}$ , 28–30%  $\text{NH}_3$ ), [2-(Di-*tert*-butylphosphino-methyl)-6 (diethylaminomethyl) pyridine] carbonyl chlorohydrido ruthenium (II) (Milstein catalyst I, precursor of Milstein Catalyst II), potassium *tert*-butoxide ( $\text{KO}^t\text{Bu}$ ), methanol (MOH), 1-propylamine ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ ), butylamine ( $\text{CH}_3(\text{CH}_2)_3\text{NH}_2$ ), hexylamine ( $\text{CH}_3(\text{CH}_2)_5\text{NH}_2$ ), benzylamine ( $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ ), ethylenediamine ( $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ), and hydrazine hydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ) were all received from Sigma-Aldrich and used without further purification. The purity of  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$  is 99.999%. The water used in all reactions was obtained by filtering through a Millipore system. Asymmetric porous alumina tubular supports were supplied by Inopor Co. The inner and outer diameters and the length of the tubes are 7, 10 and 35 mm, respectively, and the nominal pore size of the surface layer is ~100 nm.

### 2.2. Preparation of Pd-Ag/ceramic membrane

The Pd-Ag/ceramic membranes were prepared by the Ag-controlled electroless co-plating of Pd and Ag [3,33]. Before plating the supports were cleaned sequentially by ethanol, 4% aqueous KOH solution and deionized water and well Pd seeding activated [34]. In a typical process, 60 mL Pd bath was loaded into a glass container and 15 mL Ag bath in a syringe. The Pd bath contain 3.9 mmol/L  $\text{PdCl}_2$ , 5.0 mol/L  $\text{NH}_4\text{OH}$  and 0.12 mol/L  $\text{Na}_2\text{EDTA}$  dissolved in deionized water, and the Ag bath contain 5.1 mmol/L  $\text{AgNO}_3$ , 5.0 mol/L  $\text{NH}_4\text{OH}$ , and 0.12 mol/L  $\text{Na}_2\text{EDTA}$  mixed in deionized water. To achieve a defect-free membrane, the plating process was conducted twice. After the first plating, the membrane was washed, dried and then annealed 10 h at 500 °C in  $\text{H}_2$ . Then the membrane was seeded again before the second co-plating. The final Pd-Ag membrane was heat-treated at 500 °C in  $\text{H}_2$  for 36 h before used for reaction.

### 2.3. Reactions in the membrane reactor

The design of the membrane reactor was previously described [3]. The tubular membrane was mounted in a custom-designed cylinder cell and sealed by graphite gasket O-rings at both ends. The space between the shell side of the membrane and the cylinder cell, which is about 2 mL, is used as the reaction chamber. The membrane surface area is approximately 6  $\text{cm}^2$ . The cylinder cell was placed inside a vertical furnace with programmable temperature controller. The reaction temperature was fixed on 140–180 °C for different reactions. In a typical reaction, methanol (1.25–5 mmol), amine (5 mmol), Milstein catalyst I (0.005 mmol),

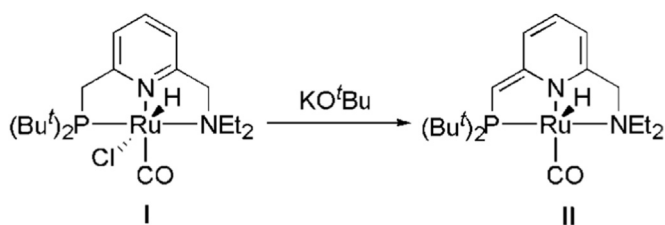


Fig. 1. The Milstein catalysts.

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