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Direct Preparation of Cyclic Imides from Amines and Carboxylic Anhydrides by Niobium (V) Oxide act as a Water-Tolerant Lewis Acid Catalyst

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Abstract: **In the 20 different types of homogenous and heterogeneous catalysts screened, niobium (v) oxide (Nb2O5) showed the highest activity for the preparation of N-phenyl succinimide by dehydrative condensation of aniline and succinic anhydride. Niobium (v) oxide (Nb2O5) was mainly used in the direct imidation of a broad range of carboxylic anhydrides with amines with different type of functional groups and could be re-used. Kinetic studies showed that the Lewis acid such as niobium (v) oxide (Nb2O5) catalyst was more water tolerant than both the Lewis acidic oxide like TiO2 and the homogeneous Lewis acid such as Zirconium (IV) Chloride (ZrCl4), which resulted in higher yields of imides through the use of niobium (v) oxide (Nb2O5).**

Keyword: Amination, ·Iimidation, Lewis acids, Niobium (v) oxide.

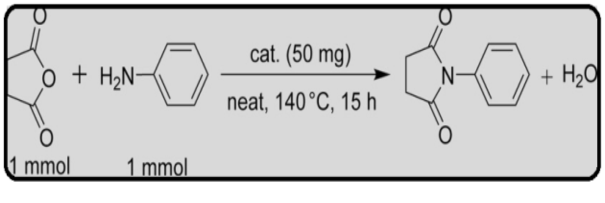
INTRODUCTION

Cyclic imides and their derivatives are a major class of substrates for hemical and biological applications; [1, 2] they are mainly used as intermediates in the industrial production of dyes, drugs, and polymers. [1x,1y, 2] but, sustainable methods for the preparation of cyclic imides from readily accessible starting materials are limited. Common methods for the preparation of cyclic imides such as dehydrative of condensation of dicarboxylic acids [3] or their anhydrides [3f, 4, 5, 6] with an amine under harsh conditions (245–3750C and 33.0 MPa) [3x,b] or under microwave heating [5, 6] and the cyclization of an amic acid with the assist of acidic agents or in the presence of an excess amount of a promoter (Such as Lewis acid, base, dehydrating reagent). These methods suffer from drawback like low atom effectiveness, limited substrate scope, production of stoichiometric amounts of by products, and the need for special procedures (such as microwave heating). New synthetic route from halides,[7] alkynes,[8] aryl boronic acids,[9] aromatic amides,[10] aliphatic amides,[11] cyclic amines [12] and nitriles,[13] have been developed, but these homogeneous catalytic methods have some limitations like low atom effectiveness, narrow substrate scope, the use of toxic chemicals or additives, and difficulties in catalyst/product separation and catalyst reuse. For example, a reusable heterogeneous catalytic system of Pd/C [8d] suffers from the require for the utilize of halides and CO as less environmentally benign agents. One of the most efficient synthesis routes to cyclic imides by de-hydrogenative coupling of diols and amines catalyzed by a Ru complex [1x, 14] still suffers from limited substrate scope of the diols and amines.

Catalytic synthesis of cyclic imides by condensation of cyclic anhydrides with amines is one of the most popular routes. A few catalytic schemes performed with the use of SiO2 or TaCl5 [15x, y] or 1,4-diazabicyclo [2.2.2] octane (DABCO)[15z] are reported to synthesize cyclic imides from cyclic anhydrides with amines. These process [15] suffer from some disadvantages, such as limited substrate scope, no results on catalyst re-use, and the need for high catalyst loadings and particular process (e.g., microwave heating). [15x, y] Potentially, the reaction can be catalyzed by a Lewis acid, but the co-presence of water as a by-product can stifle Lewis acidity by hindering co-ordination. Stimulated by recent reports that numerous metal oxides, like niobium (v) oxide,[16x] act as water-tolerant Lewis acid catalysts,[16] we newly reported that niobium (v) oxide acts as a water-tolerant Lewis acid catalyst for the direct imidation of esters with amines[17] and the direct amidation of dicarboxylic acids with amines.[18] We reported our preliminary results on the synthesis of cyclic imides from cyclic anhydrides,[18] but detailed catalytic properties such as substrate span and kinetic revise was not accounted. In this time, we report a common catalytic method for the direct synthesis of cyclic imides from cyclic anhydrides with ammonia under solvent-free situation.

EXPERIMENTAL

Niobium (v) oxide (surface area=54 m2g¢1) was organized by calcinations of niobic acid at 500-5500C for 180 minutes; the Lewis acid characteristics of niobium (v) oxide are accounted in us before studies. [17–19]. As listed in Table 01, 20 different types of heterogeneous and homogeneous catalysts were screened for the model imidation of equimolar amounts of succinic anhydride and aniline under solvent-free situation at 1450C for 14 h (Table 1). Note that the reaction hardly proceeded under catalyst-free conditions (Table 1). Thus, Table 1 shows the results of catalytic imidation. Initialy, we screened 12 different types of simple metal oxides (Table 1,). Amongst the metal oxides tested, niobium (v) oxide showed the highest yield (90%) of the corresponding imide, N phenyl succinimide. The hydrate of niobium (v) oxide called niobic acid (Table 1), gave a lower yield (22-25 %) than niobium (v) oxide Two of the oxides having Lewis acidity (ZrO2 and TiO2)[19, 20] showed moderate yields of 60–65% (Table 1). Other oxides such as SnO2, g-Al2O3, SiO2, and CaO showed low yields of 10–45 %. Next, we tested conventional solid acids such as a Lewis acidic clay, Fe+++-mont (Table 1), HBEA zeolite (Table 1) and water-tolerant Brønsted acid catalysts including HZSM5 zeolite with a SiO2/Al2O3 ratio of 300 (Table 1) and commercial acidic resins (Table 1).[21] These solid acids gave low to moderate yields (31–60%) of Nphenylsuccinimide. lastly, we tested homogeneous Lewis acids [22] (Table 1) including the water-tolerant Lewis acid [22x, y] scandium (III) trifluoro methane sulfonate [Sc (OTf)3; Table 1].



Entry	Catalyst	Yield (%)
01	Blank	Less than 1
02	Niobium (v) oxide	92
03	Niobic acid	20
04	ZrO_2	63
05	TiO_2	60
06	SnO_2	47
07	Ta_2O_5	40
08	ZnO	41
09	Al_2O_3	20
10	SiO_2	17
11	CeO_2	14
12	MgO	16
13	CaO	10
14	Fe^{+++}	30
15	HZMS (zeolites)	61
16	HBEA	41
17	Amberlytes	30
18	SiO_2 (nafion)	45
19	$ZrCl_4$	45
20	Sc $(OTf)_3$	35
21	$HfCl_4$	20

These homogeneous catalysts gave low yields of the product (18–45%). With the most effective catalyst (i.e., niobium (v) oxide), we tested the model reaction in the absence and in the presence of different solvents (Table S1, Supporting Information). We found that if the reaction was performed under solvent-free conditions, the product was obtained in a higher yield than if the reaction was performed in a solvent like toluene (or o-xylene). To talk about a possible reason why., niobium (v) oxide showed high catalytic activity for the model reaction of succinic anhydride with aniline, we studied kinetic experiments. Initialy, we measured initial rates of imide formation in the absence and in the presence of water (01, 03, and 05 mmol) by using 50 mg of the catalysts. Two heterogeneous Lewis acid catalysts (such as Nb_2O_5 and TiO_2) and a homogeneous Lewis acid catalyst (such as $ZrCl_4$) [22x] were selected for comparative purposes.

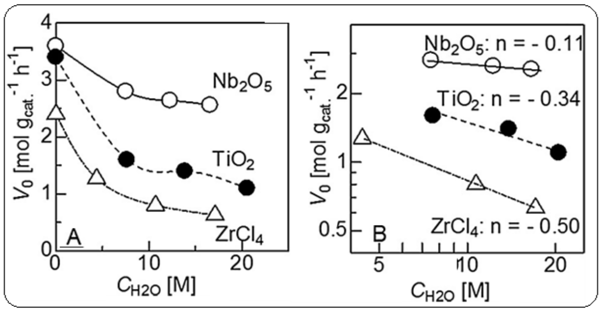


Figure 1. Initial rate for imidation of succinic anhydride (1 mmol) with aniline (1 mmol) in the presence of H_2O

(0, 1, 3, and 5 mmol) catalyzed by 50 mg of Nb_2O_5, TiO_2, or $ZrCl_4$ as a function of the initial concentration of water. Note that the rates were measured under conditions for which the conversions were below 40 %. Figure 1x plots the reaction rates as a function of the initial concentration of H_2O. For all catalysts, the addition of water decreased the reaction rate, and the rate was lower at a higher concentration of water. Figure 1b shows double logarithmic plots for the results in the presence of H_2O in the initial mixture, in which the slope of the line corresponds to the reaction order with respect to water. The reaction orders are ¢0.11, ¢0.34, and ¢0.50 for Nb_2O_5, TiO_2, and $ZrCl_4$, respectively, which clearly indicates that the negative impact of H_2O increases in the order $Nb_2O_5<TiO_2<ZrCl_4$.

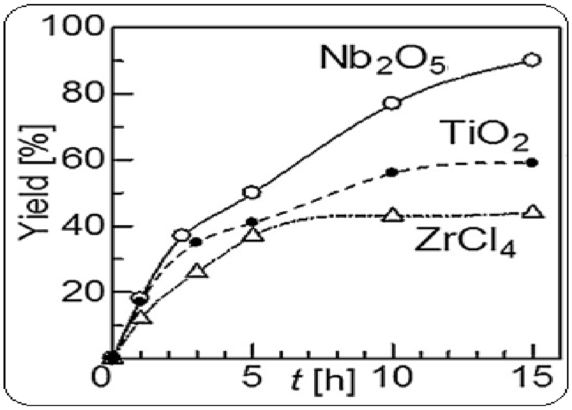
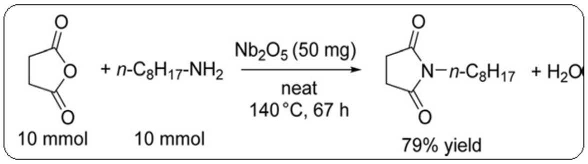


Figure2. Time–yield profiles for the imidation of succinic anhydride (1 mmol) with aniline (1 mmol) catalyzed by 50 mg of Nb_2O_5, TiO_2, or $ZrCl_4$.

Figure 2 compares the time–yield profiles for the imidation reaction in the absence of H_2O. The initial slopes for Nb_2O_5, TiO_2, and $ZrCl_4$ don't markedly depend on the catalyst, but the final yield after 15 h depends mainly on the catalyst. The yield for the Nb_2O_5- catalyzed reaction monotonically improved with time, while the yields for the TiO_2- and $ZrCl_4$-catalyzed reactions stop to rising. Considering that water is produced during the dehydrative condensation reaction, jointly with the result that the negative effect of water increases in the order $Nb_2O_5<TiO_2<ZrCl_4$ (Figure 1), the result in Figure 2 clearly indicates that the H_2O molecules formed during the reaction inhibit the Lewis acid catalysis of TiO_2 and $ZrCl_4$, On the other hand the H_2O molecules do not markedly inhibit the Lewis acid catalysis of Nb_2O_5. Thus, Nb_2O_5 is a more water-tolerance Lewis acid catalyst than TiO_2 and $ZrCl_4$.

Subsequently, we studied the efficiency of the Nb_2O_5-catalyzed imidation of carboxylic anhydrides along with amines. The outcome of a gram-scale reaction is shown in Scheme 1. The reaction of succinic anhydride (10 mmol) with n-octylamine (10 mmol) in the presence of Nb_2O_5 (50 mg) for 67 to 68 h to give the corresponding imide in 79.0 % yield. earlier, we reported the number of surface Lewis acid sites on the Nb2O5 catalyst by pyridine ad-sorption IR spectroscopy at 200-210^0C.[17, 19] The turnover number (TON) with respect to the Lewis acid sites of Nb_2O_5 (0.056 mmolg¢1) was calculated to be 2820.



Scheme 1. A gram-scale reaction of succinic anhydride with n-octylamine in the presence of Nb_2O_5.

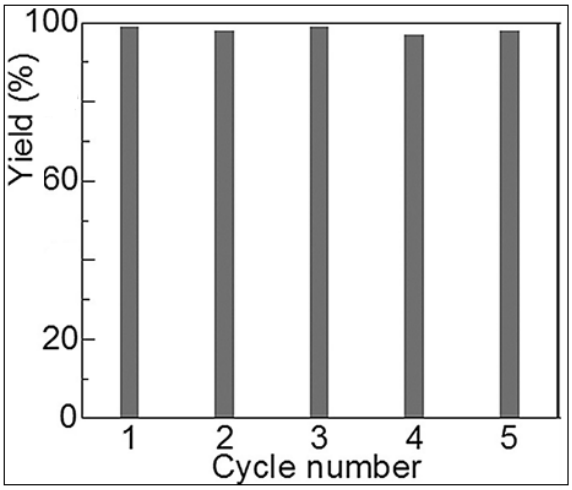
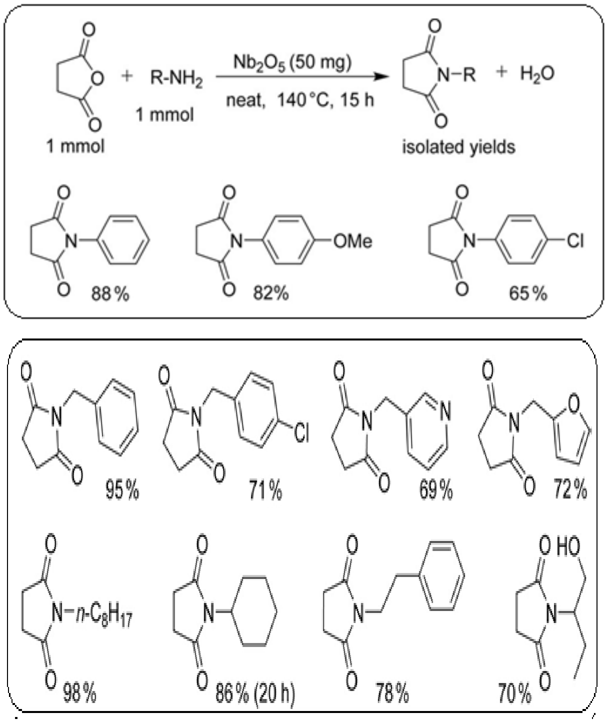


Figure 3. Reuse of Nb_2O_5 for the imidation of succinic anhydride with n-octylamine under the conditions shown in Scheme 2

Figure 3 shows the reusability of the Nb_2O_5 catalyst for the imidation of succinic anhydride (1 mmol) with n-octylamine (1 mmol) over 15 h. After the reaction, 2-propanol (4.0 mL) was added to the mixture, and the catalyst was separated from the mixture by centrifugation, follow by washing with acetone and drying at 90^0C for 180 min. The recovered catalyst was reused over four cycles without a marked reduce in the yield of the product. Analysis of the solution by inductively coupled plasma atomic emission spectroscopy (ICP-AES) confirmed that the content of Nb in the solution was below the detection limit. From the results, we can conclude that Nb_2O_5 is as a reusable heterogeneous catalyst for the title reaction.

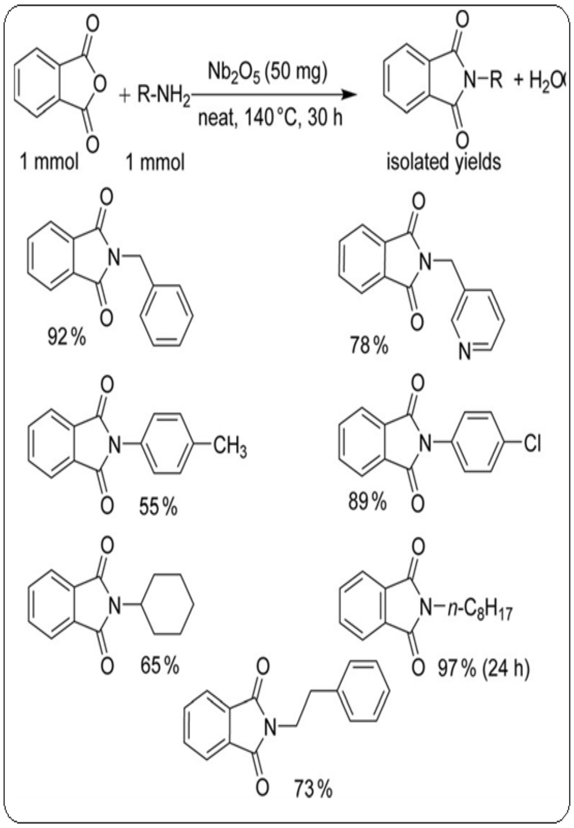
Lastly, we studied the substrate scope for the present catalytic system. Scheme 2 clearly shows the results of the imidation of succinic anhydride (1 mmol) with different type of amines (1 mmol). Under the standard solvent-free conditions with the use of a small amount of Nb_2O_5 (0.30 mol% based on the number of Lewis acid sites on Nb_2O_5),[17, 19] the mixture was heated at 140^0C for 15 h. Anilines with different type of functional groups (e.g., H-, MeO-, Cl-) in the para position, benzylamines, heteroaromatic amines with pyridyl and furanyl groups, linear and cyclic aliphatic amines, and amines with phenyl and hydroxy groups were all converted into the corresponding N-aryl imides in good to high yields (63–97 %).



Scheme 2. Substrate scope for imidation of succinic anhydride with different amines.

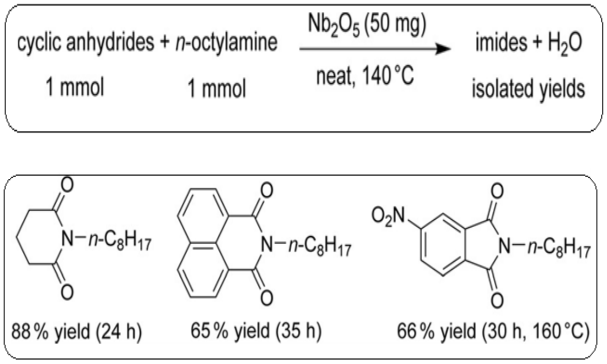
The method was also efficient for the direct synthesis of phthalimides from readily available phthalic anhydride and equimolar amounts of amines (Scheme 3). Benzyl amine, heteroaromatic amine, anilines with electron-rich and electron-poor groups, cyclohexylamine, phenylethylamine, and n-octylamine were all converted into the corresponding N-substituted phthalimides in moderate to high yields (50–95%).

Scheme 4 shows the reactions of n-octylamine with various cyclic anhydrides. Gluteric anhydride, 1,8-naphthalic anhydride, and 4-nitrophthalic anhydride were all transformed into the corresponding N-substituted cyclic imides in moderate to high yields (63–90 %). Especially, unsubstituted cyclic imides were also synthesized from cyclic anhydrides and ammonia under azeotropic reflux conditions in n-octane (Scheme 5). The reactions of succinic anhydride and phthalic anhydride in a closed stainless reactor under NH_3 pressure (0.3 MPa) at 140^0C resulted in succinimide in 79 % yield and phthalimide in 80% yield, correspondingly.

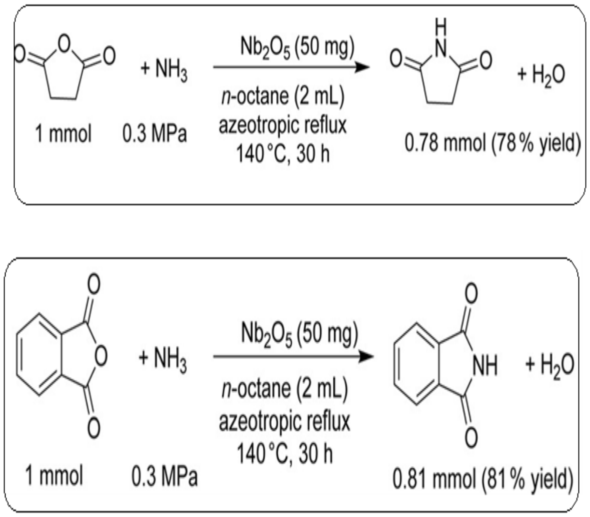


Scheme 3. Synthesis of phthalimides from phthalic anhydride and various primary amines.

Summarizing the above outcome, we can conclude that the present method involving the use of a catalytic amount of Nb_2O_5 is extensively applicable to the direct imidation of a variety of carboxylic anhydrides with ammonia or amines with various functional groups. To our information, this is the first general catalytic process for the synthesis of imides from carboxylic anhydrides and amines by using a reusable catalyst.



Scheme 4. Synthesis of N-substituted cyclic imides from cyclic anhydrides with n-octylamine



Scheme 5. Imidation of cyclic anhydrides and ammonia.

CONCLUSION

We found that cyclic imides could be synthesized directly from various cyclic anhydrides with various amines or ammonia by using niobium (v) oxide (Nb_2O_5) act as a reusable heterogeneous catalyst. This is a uncomplicated and general catalytic scheme for the synthesis of cyclic imides from readily available cyclic anhydrides and amines. Kinetic studies clearly indicated that the Lewis acid sites of niobium (v) oxide (Nb_2O_5) have a high tolerance to water, and this resulted in high catalytic activity for imidation, still in the presence of the water formed during the reaction.

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