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Ligand-free nickel-catalyzed semihydrogenation of alkynes with sodium borohydride: a highly efficient and selective process for cis-alkenes under ambient conditions

highly desirable.

we

Herein,

also be used as catalysts in combination with a nitrile functionalised imidazolium based ionic liquid.12 A copper-

catalyzed system using a N-heterocyclic carbene ligand under

molecular hydrogen enabled the semihydrogenation of

internal alkynes to cis-alkenes.13 However, these catalytic systems always make use of organic ligands, intermetallic

compounds or functional solvent, to achieve relatively high

selectivity for alkenes, which often leads to low catalytic

activity and hence lengthy reaction times. In addition, such

reactions are usually conducted using molecular hydrogen as

the hydrogen source, which must be strictly monitored to

prevent over-reduction to alkanes and also require special

equipments to operate with flammable hydrogen gas.¹⁴ In this

regard, the use of ammonia-borane as hydrogen donor has

alleviated this, but the high cost limits its further applications.

The use of the inexpensive borohydrides as reductants in the

semihydrogenation of alkynes is rather limited. Sodium

borohydride has been used as a reducing agent for the

transformation of 1,2-diphenylacetylene (DPA) into stilbene

catalyzed by a Ni(0) complex, but under forcing conditions of

80°C for 72 h.¹⁵ Thus, a reaction system involving a simple and

non-precious metal catalyst, a cheaper hydrogen source, and a

practical procedure, operating with high efficiency would be

semihydrogenation of alkynes, which operates under ambient

conditions, for the transformation of internal and even

terminal alkynes to the corresponding alkenes with great

efficiency and high selectivity in the presence of borohydrides.

In this work, the formation of the Ni NPs catalyst and the

semihydrogenation of alkynes were completed in a one-pot

process at room temperature within a few minutes. Notably,

the borohydride exhibits dual functionalities: reduction of Ni(II) to Ni NPs and hydrogen donation for the semihydrogenation. Initially, the semihydrogenation of DPA was chosen as the

model reaction to optimize the reaction conditions, including

different solvents and hydrogen donors, towards a unique

ligand-free

report a

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Received 00th January 20xx, Xin Wen,^{a,†} Xiaozhen Shi,^{a,†} Xianliang Qiao,^a Zhilei Wu,^a Guoyi Bai^{a,*}

We report a low-cost and efficient catalytic system, involving insitu generated ligand-free Ni NPs, methanol and sodium borohydride, for the semihydrogenation of alkynes under ambient conditions. This catalytic system exhibits remarkably high activity, satisfying cis-selectivity for internal alkynes, good stability and general applicability.

The selective semihydrogenation of alkynes to the corresponding alkenes is of great importance in the polymer industry as well as in the synthetic organic chemistry.¹ For decades, Pd-based catalysts have dominated this transformation.² For example, Pd/Al₂O₃ exhibited good catalytic performance in the removal of even small amounts of acetylene from ethylene streams which was a key requirement in the polyethylene industry, because its presence would decrease the polyethylene purity as well as deactivate the polymerization catalyst.³ The most famous Pd-based catalyst for this transformation is Lindlar's catalyst. However, the necessary poisons and quinoline always lead to harmful wastes and heavy metal residues in the products.⁴ In addition, overreduction to the alkane, a requirement for complex ligand, long reaction times, poor catalyst shelf-life and hence reproducibility, are features of such systems.⁵

As a cheaper alternative to the Pd-based catalysts, nonprecious metal catalysts, based on Ni,⁶ Co,⁷ Cu,⁸ and Fe,⁹ have been applied to the selective semihydrogenation of alkynes to the corresponding alkenes. For example, Richmond and coworkers reported that the cis-/trans-selectivity of nickelcatalyzed semireduction of alkynes can be controlled by a triphos ligand.¹⁰ More recently, a NiGa intermetallic nanocrystalline material with uniform particle size and controlled composition was found to be highly selective in the semihydrogenation of alkynes.¹¹ Ni nanoparticles (NPs) can

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nickel-catalyzed

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Ph		NiCl ₂ (0.4 mol% Borohydrides)		+ 7	= ^{Ph} + ^F					
Ph	Solv	ent, Room tempe	erature	Ph Ph	Ph	Ph					
Entry	Solvent	Reductant	Molar equiv. ^b	Time (min)	Conv. ^c (%)	(Z/E)/alkane ^d (%)					
1	MeOH	$NaBH_4$	0.5	115	42	(87/12)/1					
2	MeOH	$NaBH_4$	1.0	10	96	(91/8)/1					
3	MeOH	$NaBH_4$	2.0	5	98	(94/5)/1					
4^e	MeOH	$NaBH_4$	2.0	5	68	(96/4)/0					
5^e	MeOH	$NaBH_4$	2.0	30	99	(90/7)/3					
6	EtOH	$NaBH_4$	2.0	150	34	(66/30)/4					
7	dioxane	$NaBH_4$	2.0	150	8	(70/26)/4					
8	t-BuOH	$NaBH_4$	2.0	150	6	(47/37)/16					
9	EtOAc	$NaBH_4$	2.0	150	3	(69/26)/5					
10	DMF	$NaBH_4$	2.0	150	9	(52/39)/9					
11	MeOH	KBH_4	2.0	15	99	(93/6)/1					
12	MeOH	NH_3BH_3	2.0	3	52	(59/37)/4					
13	MeOH	$\mathbf{NH}_3\mathbf{BH}_3$	4.0	5	86	(29/65)/6					
14	MeOH	$\mathbf{NH}_3\mathbf{BH}_3$	8.0	3	94	(27/65)/8					
15	MeOH	H_2	-	240	0	-					
16	MeOH	$NaBH_4$	2.0	100	3	(88/12)/0					

Table 1 Semihydrogenation of DPA catalyzed by in-situ generated Ni NPs in one-not process^a

^oReaction conditions: DPA (1.0mmol). 0.4mol% Ni catalyst, solvent (8 mL), room temperature. ^bThe molar equivalent of reductant to DPA. ^cDetermined by GC. ^{*d*}Relative percent ratio of alkene (Z/E) to the corresponding alkane. ^{*e*}A two-steps method was used (ESI++). /Ni NPs was absent in the semihydrogenation.

combination of high activity and good selectivity for cisstilbene. In this one-pot process, the Ni NPs were generated in the solution, whilst the DPA molecule was hydrogenated to cisstilbene over such Ni NPs catalysts with Ni loadings as low as 0.4 mol% (Table 1). Using 0.5 molar equiv. of NaBH₄, low conversion (42%) with 87% selectivity for cis-stilbene was obtained within 115 minutes (Table 1, entry 1). When the amount of NaBH₄ was increased to 1 equiv. (Table 1, entry 2), the conversion of DPA was 96% within 10 minutes. A further increase of the amount of NaBH₄ to 2 equiv. (Table 1, entry 3), the conversion of DPA increased to 98% in 5 minutes while the selectivity for cis-stilbene increased to 94% with a high ratio of cis- and trans- ratio (Z/E = 19). In contrast, when the transformation proceeded in a two step procedure (see the ESI⁺⁺ for details), the conversion of DPA was only 68% in 5 minutes (Table 1, entry 4), but reached 99% if the reaction time was prolonged to 30 minutes (Table 1, entry 5), demonstrating that the in-situ generated Ni NPs was a highly active catalyst in the semihydrogenation of DPA. Among the solvents examined (Table 1, entries 6-10), the semihydrogenation proceeded sluggishly in non-protic solvents such as dioxane, THF, DMF, EtOAc and a weak polar solvent, t-BuOH. In contrast, the conversion increased to 34% in ethanol and markedly to 98% within 5 minutes in methanol, demonstrated the crucial role of solvents in this reaction. Particularly, the conversion of DPA and selectivity for cis-

stilbene in methanol were much higher than those in ethanol. Changing the hydrogen source to potassiunt 300rohydride, afforded a 99% conversion within 15 minutes and displayed a ph slightly lower activity than sodium borohydride, yet the selectivities roughly equivalent (Table 1, entry 11). Ammonia borane exhibited moderate reactivity compared with borohydrides in methanol in the presence of Ni NPs (Table 1, entries 12-14). Note that the ratio of cis- and trans- (Z/E) selectivity for stilbene decreased from 1.6 to 0.4 with the increase of the molar equiv. of ammonia borane from 2 to 8, but was much lower than that obtained using sodium borohydride (Table 1, entry 3; Z/E = 19), which might be attributed to the isomerization of cis-stilbene, as recently reported by Fu using a less sterically hindered Co-based catalyst in the presence of ammonia borane.7 Furthermore, the semihydrogenation of DPA did not work while using hydrogen gas under 1 atm pressure (Table 1, entry 15). In the absence of Ni NPs, the controlled experiment gave a conversion of only 3% in 100 minutes (Table 1, entry 16), demonstrating the crucial role of Ni NPs as the active catalyst. Combining the results mentioned above, sodium borohydride (2.0 molar equiv.) and methanol were chosen as the best reductant and solvent in the semihydrogenation of DPA in the presence of appropriate amount (0.4 mmol%) of Ni catalyst (Table S1, ESI++), and most importantly, the turnover frequency (TOF) value under such reaction conditions was 2940 h⁻¹, which is much higher than those of the noble metalfree catalysts and even most noble metal examples (Table S2, ESI++). Thus, we can conclude that the one-pot process including in-situ generation of Ni NPs and semihydrogenation of DPA was a remarkably efficient and selective system for cis-

The semihydrogenation of DPA under the optimized reaction conditions was also monitored by in-situ IR spectroscopy (see ESI++ for details, Fig. S1), suggesting the generation of cis-stilbene and NaB(OCH₃)₄. Trans-stilbene and 1,2-diphenylethane were not detected due to their low concentrations. Transmission electron microscopy (TEM) revealed the in-situ generated, narrowly-dispersed Ni NPs with an average size of 6.2±0.3 nm, as determined after the volatilization of methanol. These tiny Ni NPs can be isolated by simple centrifugation and reused 5 times with >91% conversion in less than 20 minutes and >91% selectivity for cisstilbene (Fig. S2, ESI++).

stilbene synthesis.



Fig. 1 TEM images of in-situ generated Ni NPs in the semihydrogenation of DPA.

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The general applicability of this catalytic system involving the ligand-free Ni catalyst, sodium borohydride and methanol was investigated with various terminal and internal alkynes under ambient conditions. The results are summarized in Table 2 and reveal that the cis-semihydrogenation pathway observed for DPA is general. Tested substrates bearing a series of functional groups, such as fluoro, chloro, bromo, cyano, ethyl, methoxyl, alkyl, ester and trifluoromethyl provided the corresponding cis-alkene products in good conversion with satisfying selectivity. Aldehydes or ketones that do not tolerate the reaction conditions¹⁶ were not included in the above functional groups. Substrates bearing a pyridine substituent afforded lower Z/E selectivity probably due to coordination with metal catalyst.⁷ Nevertheless, it should be noted that terminal alkynes with either electron-withdrawing or electrondonating groups can be smoothly hydrogenated to the corresponding alkenes with 99% conversion and >94% selectivity.

 Table 2 Nickel-catalyzed semihydrogenation of alkynes with sodium borohydride^a

Entry	Products ^b	Molar equiv.	Time (min)	Conv. ^c (%)	(Z/E) /Alkane
1	$\bigcirc \neg$	0.5	3	>99	(96)/4
2	Br	1.0	5	>99	(98)/2
3	CI	1.0	5	>99	(96)/4
4	F	0.5	3	>99	(95)/5
5	NC	1.0	3	99	(94)/6
6		0.5	5	>99	(98)/2
7	°-{	0.5	5	99	(96)/4
8	\sim	8.0	40	61	(61)/39
9	~~~~~	2.0	20	99	(94)/6
10	Solution of the second sec	1.5	5	98	(93/7)/0
11		2.0	15	99	(91/7)/2
12		3.0	15	98	(93/4)/3
13		2.0	35	>99	(85/2)/1
14		1.2	5	98	(87/4)/9

^{*o*} Reaction conditions: substrates (1.0 mmol), 0.4 mol% Ni catalyst and methanol (8 mL) at room temperature. ^{*b*} Products were identified using GC–MS and the *cis*or *trans*-isomerism were determined by NMR.

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Scheme 1 Deuterium-labeling experiments of *cis*-semihydrogenation of DPA.

То gain mechanistic insights, deuterium-labeling experiments were conducted to verify the hydrogen source in the alkene product. When NaBD₄ was used as the reductant in the semihydrogenation of DPA, the cis-stilbene was monodeuterated in the presence of Ni NPs catalyst (Scheme 1a). Likewise, it was monodeuterated when CH₃OD was used as the solvent, as presented in Scheme 1b. Conversely, dideuterated cis-stilbene was isolated when the reaction was carried out using NaBD₄ as the reductant in CH₃OD (Scheme 1c). These results therefore demonstrated that the two extrinsic hydrogen atoms in cis-stilbene should derive from the B-H of borane (hydride) and the O-H of methanol (proton), respectively. Furthermore, the nature of the byproduct containing boron can give significant information about the mechanism. Thus, the direct ¹¹B NMR spectrum was then recorded for a reaction mixture of DPA semihydrogenation, which was carried out in methanol-d⁴ in the presence of NaBH₄ as reductant. Two peaks at 3.1 and -43.8 ppm, which were respectively assigned to NaB(OCD₃)₄ and NaBH₄, were observed in the ¹¹B NMR spectrum (see ESI⁺⁺), revealed that NaBH₄ was converted into NaB(OCD₃)₄, in accordance with literature data.¹⁷ However, monomethoxy, dimethoxy and trimethoxy borate salts were not detected in the reaction mixture. The formation of the tetramethoxyl borate salt indicated that the hydroxyl group in methanol was crucial in the protonation of triple bond. Combing the results of deuterium-labeling experiments and ¹¹B NMR data, we propose that the catalytically active H, derived from NaBH₄, was first generated on the surface of the Ni catalyst. Subsequently, the catalytically active, nucleophilic H would attack the triple bond of alkyne, whilst the secondary protonation of the triple bond by the H, derived from -OH of methanol, would afford the cis-alkene, as presented in Scheme 2. In turn, the residual H of B-H and the H of -OH were delivered to the alkyne, whilst the methoxyl of methanol reacted with B of B-H, producing another 3 molecules of alkene and the by-product NaB(OCH₃)₄ finally, as verified by the ¹¹B NMR spectrum. As depicted in Scheme 2, ideally 1 molecule of NaBH₄ can reduce 4 molecules of alkyne in methanol. Indeed, only part of the NaBH₄ was utilizable in the semihydrogenation due to the generation of hydrogen gas that escaped from the solution, as previously reported by other groups in the hydrogen production from sodium borohydride in alcohol-containing solutions.18 It must be pointed out that the generated hydrogen gas was not the hydrogen source in the semihydrogenation, which was proven by

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the zero conversion of DPA with hydrogen gas as the only hydrogen source (Table 1, entry 15).



Scheme 2 The mechanism for the *cis*-semihydrogenation of alkynes by the sodium borohydride in the presence of Ni NPs.

In summary, we present a novel catalytic system for the semihydrogenation of internal and terminal alkynes under ambient conditions. The catalytic system involving ligand-free Ni NPs, methanol and sodium borohydride, exhibited remarkable high activity, satisfying *cis*-selective and general applicability. This protocol can accomplish in a cheaper, more practical manner and is a compelling alternative to the semihydrogenation of alkynes over the existing catalytic systems.

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