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Transfer Hydrogenation of Alkynes into Alkenes by Ammonia Borane over Pd-MOF Catalyst

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Ammonia borane with both hydridic and protic hydrogens in its strcture acted as effcient transfer hydrogenation agent for selective transformation of alkynes into alkenes in non-protic solvents. Catalytic synergy between μ_3 -OH groups of UiO-66(Hf) MOF and Pd active sites in Pd/UiO-66(Hf) furnished elusive >98% of styrene selectivity and full phenylacetylene conversion at room temperature. Such performance is not accessible by Pd+UiO-66(Hf) physical mixture or by commercial Pd/C catalyst.

Selective conversion of alkynes into alkenes by avoiding over-hydrogenation has received considerable attention because of its industrial importance.¹ Very few catalytic studies that deals with high selectivity towards semihydrogenation products have been reported using hazardous pressurized H₂ as hydrogen source.² In recent times, transfer hydrogenation has emerged as a safer and viable alternative to replace hazardous pressurized H₂ gas in hydrogenation reactions.³ Transfer hydrogenation involves the addition of hydrogen to a molecule from a source other than gaseous H₂. A range of hydrogen transfer reagents such as isopropanol,⁴ formic acid,⁵ hydrazine,⁶ benzothiazoles,⁷ sodium borohydride⁸ and triethylsilane ⁹ have been employed with a better chemo- and stereo-selectivities.

Recently, ammonia borane ($H_3N \cdot BH_3$, AB) has emerged as an interesting transfer hydrogenation agent because of its ability to participate in double H transfer reactions.^{10, 11} AB is

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Scheme 1: Transfer hydrogenation of phenylacetylene under uncatalyzed and catalyzed conditions using ammonia borane as a hydrogen source.

an interesting Lewis acid-base adduct that contains both hydridic and protic hydrogens in its structure. It is a quite stable compound and safer to handle at ambient conditions. Because of the presence of 19.6 wt % of hydrogen content, the compound has received substantial attention as a solid state hydrogen storage medium.¹² AB is found to participate in double H transfer reactions with activated double bonds(C=N, activated C=C, C=O) through six membered transition state that enables control over stereo- and chemo- selectivity.¹⁰

Transfer hydrogenation of alkynes with AB has been studied using homogeneous catalysts.13 However, only very few heterogeneous catalysts namely, Au/TiO₂, Pt/TiO₂, Cu₂O, and Ni nanoparticles have been reported for this reaction. ¹⁴ In these four studies, transfer hydrogenation has been carried out in protic solvents (water/alcohols). It is noteworthy that, unlike in protic solvents, AB dehydrogenation in non-protic solvent lends a possibility for regeneration of the starting material from the spent BNH_x products.^{15, 16} In view of this, we explored transfer hydrogenation in a non- aqueous medium with AR under both non-catalytic/catalytic conditions(Scheme1).

Metal-organic frameworks (MOFs) with well defined porosity and exceptional surface areas have attrracted much attention as a new class of tunable hetrogenaous catalysts.¹⁷ To facilitate transfer hydrogenation with AB, we supported Pd

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nanoparticles onto UiO-66(Hf) {Hf₆O₄ (OH)₄[(O₂C)-C₆H₄-(CO₂)]₆} MOF with a objective of bringing μ_3 -OH groups and Pd sites in close proximity. As AB is known for its hydrogen bonding ability such arrangment of active sites can have pronounced effect on transfer hydrogenation.

Table 1. Transfer hydrogenation of phenylacetylene using different hydrogen sources.

S.No	Source	Phenylacetylene conv.(%)	Styrene sel.(%)
1	EtOH	0.0	-
2	Isopropanol	0.0	-
3	нсоон	0.0	-
4	H ₂	0.0	-
5	$NaBH_4$	4.5	99.9
6	N_2H_4 H_2O	7.5	99.9
7	NH_3BH_3	99.9	99.9

[a] Reaction conditions: 0.50 mmol of hydrogen source, 1 mL of 1, 4-dioxane and 0.25 mmol of PA at 110 $^{\circ}C$ for 1h.

Initially, we have screened various transfer hydrogenation agents (Table1) for semi hydrogenation of phenylacetylene (PA) in catalyst free conditions at 110 °C in a non-aqueous solvent (1, 4- dioxane). The reactions were carried out in a closed system. As evident from Table 1, traditional transfer agents isopropanol, ethanol, and formic acid did not show any PA conversions and inferior PA conversions have been observed with NaBH₄ and N₂H₄·H₂O. With AB as a hydrogen source, full conversion of PA has been realized with a remarkable >99 % ST selectivity (Figure S3, Figure S4). It could be noted that achieving higher ST selectivity (>95 %) at full PA conversions is a challenge in case of metal-catalyzed hydrogenation reactions (with H₂).¹⁸ Further, ST was subjected to transfer hydrogenation directly under same reaction conditions as PA. We did not observe formation of any ethyl benzene in this reaction. This suggests that AB selectively transfers hydrogen to C=C bond over C=C under our reaction conditions. Further, when reactions were carried out in protic solvents (Section S5, Figure S2) such as water and ethanol, the PA conversion were only 0% and 7.0%, respectively. This justifies use of non-protic solvents for uncatalyzed transfer hydrogenation.

As evident from Figure 1a, 110 °C is found to be the optimized temperature. Temperatures like 100-110 °C are very close to dehydrogenation temperatures of neat AB. Therefore, at these temperatures, there will be two competitive processes, one transfer hydrogenation reaction and other self dehydrogenation of AB itself. As a result, excess AB (PA: AB =2) was needed to realize full PA conversions (Figure 1b). The reaction proceeded to completion in about 15 min (Figure 1c). The ST selectivity remained high (>99 %) at all conversions. Prolongation of reaction time did not change the ST selectivity. So, in contrast to metal-catalyzed hydrogenation reactions,¹⁸ a strict control over the reaction time is not necessary to maintain high ST selectivity. As expected, molecular H₂ did not react with PA (in the absence of a catalyst) under our reaction conditions. ¹⁹

To obtain mechanistic insight of the reaction, density functional theoretical (DFT) calculations were performed at M06-2X/cc-pVTZ level ²⁰ (Figure 2) which revealed an



Figure 1. Transfer hydrogenation of phenylacetylene (PA) using ammonia borane (AB) in the absence of catalyst in non-aqueous medium a) at different reaction temperatures for 1h, b) different PA/AB molar ratios at 110 °C for 1h, and c) Time resolved study at 110 °C. Reaction conditions: 0.50 mmol of AB, 1 mL of 1, 4-dioxane and 0.25 mmol of PA.



Figure 2. M06-2X/cc-pVTZ (PCM, 1, 4-dioxane) calculated structures and free energies (kcalmol⁻¹) for the reduction of phenylacetylene with NH₃BH₃. Distances on transition state structures are shown in picometer (pm) unit.

asynchronous double-H-transfer process from AB to PA ²¹ Depending upon the relative orientation of AB and PA, two possible six-membered cyclic transition states, TS1 and TS2 were located with free energy barriers of 32.6 kcal mol⁻¹ and 33.4 kcal mol⁻¹, respectively (Figure 2). The TS1 and TS2 represent B-H•••C/N-H•••C* and B-H•••C*/N-H•••C hydrogen transfer, respectively (C* = acetylenic CH). The barriers are indicative for very slow reaction kinetics, thus required 110 °C to accelerate the reaction. The reaction is thermodynamically favorable by 43.6 kcal mol⁻¹. Several

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Figure 3: a) and b) Bright field-TEM image and HR-TEM of Pd/UiO-66(Hf), c) Transfer hydrogenation of PA over different catalysts, d) Proposed mechanism for transfer hydrogenation of PA over Pd/UiO-66(Hf) through transition state and e) Pd/UiO-66(Hf) catalyst activity test for PA conversion under different hydrogen sources (AB and H₂). *Reaction conditions*: 1 mol % of catalyst (0.0027 mmol of Pd), 0.50 mmol of AB/ 0.3 bar H₂, 1 mL of 1, 4-dioxane and 0.25 mmol of PA at R.T for 30 min.

attempts to optimize an intermediate for a stepwise mechanism were unsuccessful possibly due to the absence of such minimum on the potential energy surface. We also checked the possibility of further reduction of ST to ethyl benzene. The reduction barrier of ST with AB is 36.4 kcal mol⁻¹ which is 3.8 kcal mol⁻¹ higher than the relative free energy of TS1 (Scheme S3). At 110 °C, the ST reduction barrier is very much less accessible than that of PA and this resulted in the selective formation of ST without further reduction within the reaction timescale. Further, higlighting the role played by solvent in the transferhydrogenation, incorporation of water (inplace of 1,4-dioxane) as a solvent into the computations enhanced the barrier energies of TS1 (36.0 kcal mol⁻¹).

To bring down the reaction temperature from 110 °C, we synthesized Pd/UiO-66(Hf) catalyst by depositing preformed Pd nanoparticles (3.5 ± 0.15 nm) over UiO-66(Hf) MOF surface (Figure S1). As shown in bright field transmission electron microscopy (TEM) image, Pd NPs were well dispersed onto the UiO-66(Hf) MOF surface and high resolution-TEM revealed crystalline nature of Pd nanoparticles with d-spacing corresponding to (111) plane (Figure 3(a, b)). UiO-66(Hf) MOF is quite stable and contains polarized μ_3 -OH group on its secondary building unit.²² Over Pd/UiO-66(Hf) catalyst, full PA conversion with ST selectivity of 98.5 % was noticed at room temperature in 30 min (Figure 3c, Figure S6). On other hand, over Pd+UiO-66(Hf) mixture the PA conversion was only 35.2 % (Figure 3c). This observation confirms the presence of catalytic synergy between μ_3 -OH and Pd active sites. Further, UiO-66(Zr) MOF which also has μ_3 -OH sites on its SBU smilar to UiO-66(Hf) has been explored as a support for Pd

nanoparticles (Section S8). The μ_3 -OH groups on UiQ-66(Zr) are relatively less polarized when compared to UiO 66(A4) and 26 lower oxophilicity of Zr(IV) when compared to Hf(IV). Pd/UiO-66(Zr) catalyst under same reaction conditions as above afforded only 65.2 % PA conversion (vs >99% for Pd/UiO-66(Hf)) with ST selectivity of 99.8%. This underlines the role played by μ_3 -OH group on the catalytic performance of Pd-MOF catalysts. We also carried out PA transfer hydrogenation over commercially available Pd/C catalyst (Figure 3c). It gave only 5.5 % PA conversion under same reaction conditions. Thus, Pd/UiO-66(Hf) is an efficient catalyst and superior compared to various catalysts reported for this reaction (Table S1). The presence of -OH groups next to Pd in Pd/UiO-66(Hf) can bring AB and PA in close proximity (Figure 3d). μ_3 -OH groups of MOF can favorably adsorb AB through hydrogen bonding and facile adsorption of PA over Pd surface is well document.²³ This will facilitate the transfer hydrogenation through six membered transition state and bring about catalytic synergy at the interface of Pd and MOF.

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Table 2. Transfer hydrogenation of phenylacetylene using different hydrogen sources.

S.No	Substrate	Conv.	Selectivity (%)	
•		(%)[a]	C=C	C-C
1	Phenylacetylene	>99.0	98.5	1.5
2	Ethynylcyclohex	99.5	86.4	13.6
	ane			
3	1-hexyne	99.6	95.1	4.9
4	3-hexyne	14.5	> 99.8	nd
5	1-hexene	1.5	-	100
6	Styrene	5.1	-	100
7	Cyclohexene	nd	-	nd

[a] Reaction conditions: 1 mol % of catalyst (0.0027 mmol of Pd), 0.50 mmol of hydrogen source, 1 mL of 1, 4-dioxane and 0.25 mmol of substrate at R.T for 30 min.(nd- not determined).

On other hand, use of H_2 (0.3 bar, equivalent of total hydrogen content in AB) over Pd/UiO-66(Hf) under same reaction conditions, yielded 47.5 % PA conversion and 55 % of ST selectivity. This observation clearly justifies the use of AB over H_2 .

As shown in table 2, other alkynes also showed preference for semihydrogenation product with AB over Pd/UiO-66(Hf). Further, consitent with observed selectivty, transfer hydrogenation of alkenes with AB (1-hexene styrene and cyclohexene) under same reaction conditions did not show any appreciable conversions. The Pd/UiO-66(Hf) catalyst found to be recyclable up to three cycles and stable (Section S9).

Conclusions

In conclusion, the use of AB as hydrogen source instead of H₂ provided excellent selectivity towards semihydrogenation products. Contrary to protic solvents, transfer hydrogenation with AB in 1,4-dioxane under uncatalyzed conditions(around 110 °C) afforded >99% selectivity towards styrene. The cooperativity between μ_3 -OH sites of MOF and Pd active sites

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in Pd/UiO-66(Hf) catalyst brought down the reaction temperature to room temperature. Overall, our approach paves a way for development of sustainable process for selective conversion of alkynes into alkenes.

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Conflicts of interest

There are no conflicts to declare.

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