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Journal Name

ARTICLE

Room-Temperature Transfer Hydrogenation and Fast Separation of Unsaturated Compounds over Heterogeneous Catalysts in an Aqueous Solution of Formic Acid

Ling-Hong Gong, Yi-Yu Cai, Xin-Hao Li*, Ya-Nan Zhang, Juan Su and Jie-Sheng Chen*

The facile conversion of olefins and unsaturated biomass to saturated compounds is achieved over heterogeneous catalysts composed of noble metal nanoparticles and carbon nitride. Reactions could proceed smoothly at room temperature in water by using formic acid as the hydrogen source. The reusability of such a hybrid catalyst is high due to the strong Mott-Schottky effect between the metal nanoparticles and carbon nitride support. The fast and automatic separation of the as-formed saturated hydrocarbons from water combined with the mild reaction condition and the excellent reusability of catalysts make the catalytic process a highly "green" path for hydrogenation of unsaturated compounds and biofuel upgrading.

Introduction

Hydrogenation of unsaturated carbon-carbon bonds is a vital reaction in organic chemistry, which has been used in the synthesis of fine chemicals, particularly of flavor and fragrance chemistry and pharmaceuticals.[1] In conventional methods, hydrogenation of the C=C bonds was mainly conducted in gas phase with excess amount of hydrogen gas (> 25 times). Gaseous hydrogen is difficult and dangerous to handle due to its hazardous properties. As an alternative, transfer hydrogenation of unsaturated bonds by using stable and abundant hydrogen sources is safer and environmentally benign.

Among the hydrogenation of unsaturated C=C bonds, upgrading furfural and its unsaturated derivatives into saturated hydrocarbons with better thermal stability and low toxicity is the key step to realize the practical application of furfural in the realm of biofuels and sustainable energy supplies.[2-5] Furfural is an important intermediate from biomasses, because it may be used to produce furan chemicals, chemical solvents, and liquid biofuels.[4] However, furfural by itself is toxic and thus not suitable for large-scale applications as fuels or solvents. In addition, furfural and its corresponding derivative compounds, including furfuryl alcohol and 2-methylfuran, cannot be directly used as motor fuel because they tend to polymerize into solid byproducts at elevated temperatures due to the presence of unsaturated carbon-carbon bonds.[5]

The main purpose of biofuel upgrading is to increase the quality of the fuels by removing the oxygen and increasing the hydrogen/carbon ratios. Taking furfural for example, hydrodeoxygenation[6] (HDO) and hydrogenation are the two essential processes (Figure 1) to gain high quality biofuels, which can be used directly as a motor fuel or a gasoline additive in P Series type fuels.[5] Again, green and cost-effective methods for

hydrogenation of furfural, furfuryl alcohol or 2-methylfuran are highly required for the real use of biofuels at low cost.
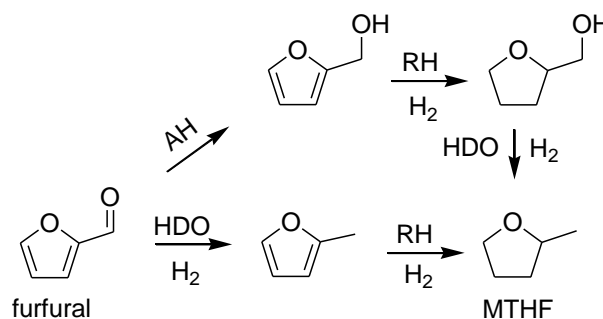

Figure 1. Typical conversion paths of transforming furfural to 2-methyltetrahydrofuran (MTHF) via hydrodeoxygenation (HDO) and ring hydrogenation (RH).Aldehyde hydrogenation (AH) of furfural was sometimes involved.

The science of green chemistry was developed to meet the increasing demand for environmentally benign chemical processes.[7-12] Within this regard, the combination of efficient and reusable catalytic protocols for transfer hydrogenation reactions under mild conditions and environmentally friendly solvents is the most important issue. Herein, we report the application of the Mott-Schottky catalyst based on g-C_3N_4 supported noble metal nanoparticles (M/CN) in room-temperature hydrogenation of 2-methylfuran and other compounds with C=C bonds. All reactions were conducted in an aqueous solution of formic acid (FA) in ambient atmosphere. The heterogeneous Mott-Schottky catalyst can

be reused for tens of circles without obvious loss of its catalytic activity.

With respect to catalytic reactions, metal nanoparticle-based heterogeneous catalysts have good reusability as compared with homogeneous ones. Current heterogeneous catalysts[8] available for transfer hydrogenation of C=C bonds are mainly carbon supported noble metal catalysts[9] with low efficiency. Most examples of heterogeneous catalytic reactions were conducted in organic solvents, whilst high temperature and/or sonication were usually required to ensure a high conversion.[1,8,9] In order to improve the catalytic activity of noble metal nanoparticle based catalysts, there have been many attempts to rationally control the sizes, shapes and/or contents of alloying metals.[10] Critical control of the structure and content at the nanometer scale required very complicated fabrication processes, which are not suitable for industrial applications. Thus, current efforts have been turned towards exploiting useful support effects to improve both the dispersion and the activity of the embedded metal nanoparticles.[7]

Results and discussion

Table 1. Study of the reaction conditions[a]

$$\text{styrene} \xrightarrow[\text{25 °C}]{\text{Catalyst/HCOOH}} \text{ethylbenzene}$$

Entry	Catalyst	Solvent	C.(%)[b]	S. (%)[b]
1	-	H_2O	–	–
2	Pt/CN	H_2O	trace	–
3	Au/CN	H_2O	–	–
4	Ag/CN	H_2O	–	–
5	Pd/CN	H_2O	>99.9	>99.9
6[c]	Pd/CN	H_2O	–	–
7[d]	Pd/CN	H_2O	>99.9	>99.9
8[e]	Pd/CB	H_2O	–	–
9[f]	Pd/N-LC	H_2O	–	–
10	Pd/SiO$_2$	H_2O	4.44	>99.9
11	Pd^{2+}/CN	H_2O	–	–
12	CN	H_2O	–	–
13	Pd/CN	ethanol	57.98	>99.9
14	Pd/CN	CH_3CN	>99.9	>99.9
15	Pd/CN	ethyl acetate	>99.9	>99.9
16	Pd/CN	DMF	32.70	>99.9
17	Pd/CN	THF	76.02	>99.9

[a] Standard conditions: 2.5mL of H_2O, 0.1mmol of styrene, 0.3 mmol of FA, 10 mg of catalyst, 15 min, T=298 K. [b] Conversions (C.) and selectivity (S.) were determined by GC by using a FID detector. [c] Without FA. [d] The reaction was conducted in N_2. [e] CB: carbon black. [f] N-LC: Nitrogen-doped layered carbon.

We recently introduced a series of M/CN dyads as Mott-Schottky catalysts, the activity of which were significantly promoted by the varied electron density at the interface of rectifying metal-semiconductor contact.[7,14] Extending the concept of Mott-Schottky catalyst to organic reactions is of great importance in the search for both laboratory-scale and industrial synthesis. FA was selected as a possible hydrogen source here due to its low toxicity, low cost and high stability. More importantly, FA can be obtained in large quantities via hydrogenation of waste carbon dioxide from industry, biomass processing and artificial photosynthesis.[1,7] Consequently, FA

can be considered as a sustainable mediate for hydrogen storage, promising its application as a sustainable choice of hydrogen resource for organic synthesis.

A series of M/CN catalysts (M= Ag, Au, Pd and Pt) and control samples were fabricated via a modified wet impregnation method (for detailed methods, see supporting information).[12-14] The powder X-ray diffraction (PXRD) patterns (Figure S1) and transmission electron microscopy images (TEM, Figure S2) of the M/CN materials confirmed the formation of metal nanoparticles on the surface of CN. The work functions of most noble metals are lower than that of g-C$_3$N$_4$, making it possible to construct rectifying contact between g-C$_3$N$_4$ and noble metals. However, Pd/CN offered the highest conversion (entry 2-5, Table 1) due to the high activity of Pd in activating the hydrogen source FA, which has been demonstrated in both experimental and theoretical results.[7] Pd/CN as the best catalysts here was thus selected for the following reactions.

We further optimized the molecular ratios of FA and substrate for hydrogenation of styrene over Pd/CN in water at room temperature. The total conversion of styrene to ethylbenzene was achieved when three equivalents of FA or more was used (Figure S3). Blank experiments indicated that the reduction of styrene could not proceed without the presence of catalyst or FA (Table 1, entry 1, 6). Various solvents were screened over Pd/CN (Table 1, entry13-17) to test the solvent effect. The survey shows that water, CH_3CN and acetic ester provided the same outcome, which is better than those of ethanol, DMF and THF. However, as compared with CH_3CN (or acetic ester) which is stimulating and nocuous, water is more environment-friendly and cheaper, meeting the requirements of green chemistry. It is worth noting that the transfer hydrogenation reactions of C=C bonds over heterogeneous catalysts in the literature could only be conducted in toluene or mixture of toluene and other solvents, where high temperature (or sonication) and protection gas were required to assure the catalytic performance.[1,11]
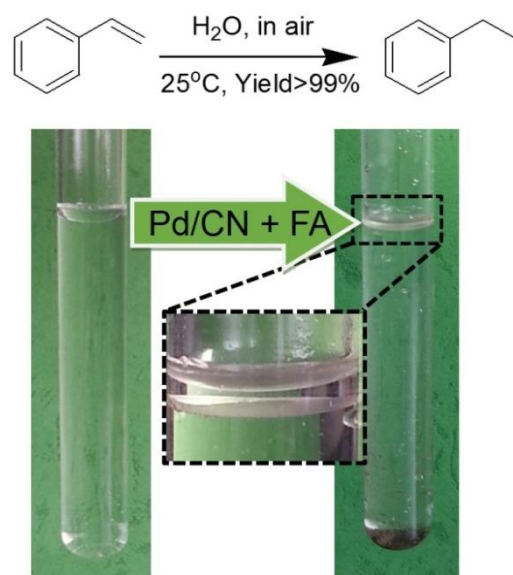

Figure 2. The fast separation of ethylbenzene after the hydrogenation reaction of styrene. The as-formed ethylbenzene was separated automatically from the water phase after reaction within 10 minutes. The solid catalyst was precipitated automatically in the bottom and separated facily from the oil phase via filteration or decantation. Reaction condition: 10 mmol of styrene, 250 mL of H_2O, 30 mmol of FA, 500 mg of Pd/CN, 298K.

For practical applications, fast separation of final products and catalysts from mother solution is an important aspect to be considered for reducing the additional cost of purification of the final products. The target products here are saturated hydrocarbon with rather low solubility in water, making it possible to separate the oil phase from the aqueous solution used here. The as-formed ethyl benzene (Figure 2 and Figure S4) can be separated automatically after reaction again revealing the advantage of our green catalysis system by using only water and FA as the reactants. Moreover, the heterogeneous catalyst can also be separated from the mother solution via simple decantation for further use in the following reactions.

A)

B)

C)
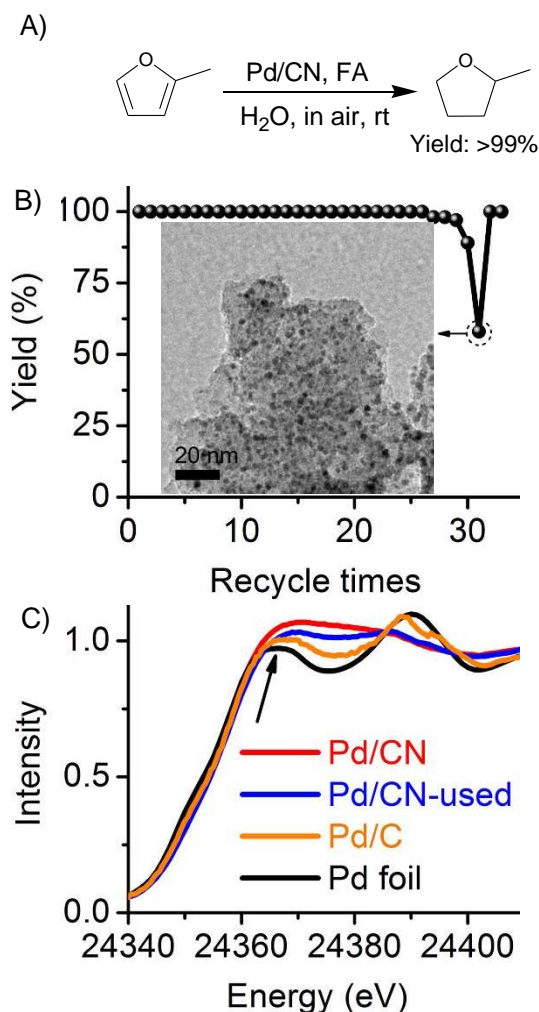
Figure 3. (A) The path of hydrogenation of 2-methylfuran to 2-methyltetrahydrofuran (MTHF). Reaction condition: 0.1 mmol of 2-methylfuan, 2.5 mL of H_2O, 0.5 mmol of FA, 10 mg of Pd/CN, 298K.(B) Reuse of Pd/CN catalyst for transfer hydrogenation of methylfuran. Reaction conditions: 0.1 mmol of methyl furan, 5 mL of H_2O, 0.5 mmol of FA, 20 mg of catalyst, 298K, 30 min. Regeneration of Pd/CN-used catalyst was conducted after 31st run by dispersing the separated catalyst in 0.1 M NaOH for 12 h followed by completely washing with water. (C) The EXAFS Pd K-edge spectra of Pd/CN and Pd/CN-used; the intensity of white line (arrow) reflected the enriched electron intensity of supported Pd NPs Inset (B): the TEM image of deactivated catalyst (Pd/CN-used) after 31 runs.

After knowing the activity of Pd/CN in reducing C=C bonds by FA, we thus turned towards the hydrogenation of 2-methylfuran to 2-methyltetrahydrofuran (MTHF), which is the key step for

increasing the hydrogen/carbon ratios and thus transforming the biomass (furfural) to renewable biofuel (MTHF) (Scheme 1). Recently, Pd nanoparticles modified with certain organic tail ligand were utilized as high selective catalysts for the formation of methylfuran.[15] Interestingly, Pd/CN nanocatalyst can further catalyze the hydrogenation of 2-methylfuran which is a conjugated diene and gave a high yield (Figure 3A) at room temperature. Such a yield value far exceeds those over the carbon-supported Pd catalysts (Pd/N-LC[12] and Pd/C) and SBA-15-supported Pd catalyst (Pd/SiO$_2$[13]) under the same conditions (Figure S5). For Pd/CN and Pd/N-LC, the surface area, types of nitrogen functional groups, sizes of PdNPs and Pd loadings (8 wt%) are similar (Figure S6 and Table S1), excluding the structure effect of the catalysts on the catalytic performance. The fact that nitrogen-rich sample Pd/N-LC (N content: 10 at.%) also offered no conversion rather suggested that the strong adsorption of formic acid is not enough to ensure the activity of Pd/N-LC for such a transfer hydrogenation reaction here. An obvious decrease of photolumincent intensity of CN (Figure S7) after loading of Pd NPs directly indicated the charge transfer from CN to Pd metal and thus an obvious Mott-Schottky effect at the Pd-CN interface. Consequently, the superb catalytic activity of Pd/CN is attributed to Mott-Schottky effect, which has been described in our previous work concerning photocatalytic Suzuki coupling reaction and dehydrogenation of FA.[7c,14]
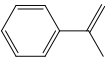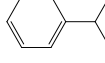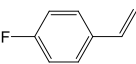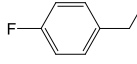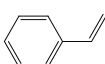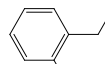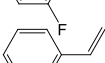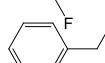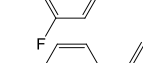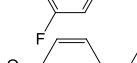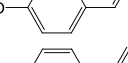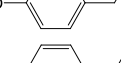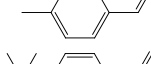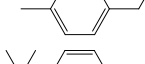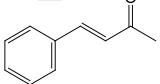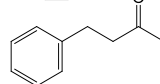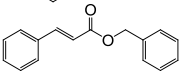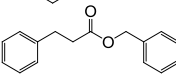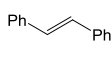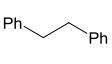
Besides high catalytic activity, the reusability and stability are also important issues for practical applications of Mott-Schottky catalysts in industry. We thus tested the catalytic performance of used Pd/CN catalyst for transfer hydrogenation of 2-methylfuran. In fact, the Pd/CN catalyst was successfully recycled without any loss of activity after at least 26 times of reuse (Figure 3B) with a simple base washing process using 0.1 M NaOH solution after each run (for experimental detail please see ESI). Pd leaching was excluded in current catalytic system by inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis with the concentration of Pd in the filtrate below the detection level of the equipment (0.1 ppm).

To further verify the stability of our catalyst, another five runs were conducted with a gradual decrease in activity. At the 31st run, the yield drops to about 60%. However, the chemical structure (Figure S8a) and morphology (Figure 3B and S8b) of both the Pd nanoparticles (Figure S9) and the CN support remained unchanged after 31 runs of catalytic reactions. We thus can exclude the effect of structural variation on the catalytic activity. As CN stays stable in FA solution, the band structur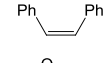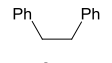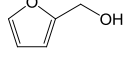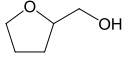e of CN was also not changed after multiple uses. Therefore, it is presumable that the interface of Pd and CN may be changed by the protonation of the surface of CN in FA solution (Figure S10). Such a protonation process is common in CN-based catalysis and photocatalysis due to the presence of terminal amino groups and of bridging nitrogen on the surface of CN.[7,14] An adsorbed layer of protons as a "contact resistance" leads to a loss of voltage or the coupled chemical potential at the metal-semiconductor interface,[7a] which was unambiguously demonstrated by the extended X-ray absorption fine structure spectra (EXAFS) analysis (Figure 3C).The enriched electron intensity of Pd nanoparticles in Pd/CN was confirmed by the highest intensity of white line in EXAFS K-edge spectra of all samples (Figure 3C). The deactivated Pd/CN (named Pd/CN-used in Figure 3B) had a lower white line, suggesting a lower electron intensity of Pd nanoparticles. Such a loss is however unwanted in our Mott-Schottky catalysts as reflected by the significant decrease in the final catalytic activity. By following this principle, deprotonating the interfacial area of used catalyst should be sufficient to recover the deactivated catalysts. Indeed, the deprotonated catalyst offered total conversion of the substrate again without obvious loss of activity in the following 2 runs (Figure 3B

and Figure S11). Again, this observation reveals the key role of the support effect, named Mott-Schottky effect as described in our previous work[7a-c] at the metal-CN interface for ensuring the catalytic performance of Pd nanoparticles. In order to demonstrate this effect, we also tested the reusability of Pd/SiO$_2$, one of the catalysts without Mott-Schottky effect, showing a lower reusability and stability (Figure S12). Such a Mott-Schottky effect can be further proved by the enhanced activity under photo-irradiation (Figure S13) for transfer hydrogenation of nitrocompounds, where the transfer hydrogenation reaction didn't consume electrons.[7a-c,14] CN supported noble metal nanoparticles can be thus considered as stable and reusable heterogeneous catalysts for practical applications.

Considering the possibility of dehydrogenation of FA over Pd/CN to release H$_2$, which can also be used to reduce C=C bonds, further control experiments were conducted to investigate the reduction path of 2-methylfuran in our catalytic system. Under fixed condition, the conversion of FA significantly rose up to at least 2.5 times after the introduction of 2-methylfuran (Figure S14). This is to say that extracting the hydrogen of FA to reduce 2-methylfuran over Pd/CN is much faster and easier than to form H$_2$ gas, which requires more energy to overcome the over potential of the chemisorbed H at noble metal surface.[16] In other words, formation and activation of hydrogen gas were not essential for the reduction of unsaturated carbon bonds here.

Table 2. Transfer Hydrogenation of Various Unsaturated Compound[a]

Entry	Substrate	Product	T(min)	C. (%)	S. (%)
1			15	> 99	> 99
2			30	> 99	> 99
3			30	98	> 99
4			30	94	> 99
5			60	94	> 99
6			30	> 99	> 99
7			60	60	>99
8[b]			15	> 99	> 99
9			60	70	> 99
10			180	56	> 99
11[c]			60	> 99	21
12			180	52	> 99
13			180	–	–
14[d]			120	64	>99

[a] Standard conditions: 2.5 mL of H$_2$O, 0.1mmol substrate, 0.3 mmol of FA, 10 mg of Pd/CN, 298K. [b] 0.5 mmol of FA was added. [c] 79 % of C$_6$H$_5$CH$_2$CH$_2$COOH was detected. [d] 0.5 mmol of FA was added, 20 mg of Pd/CN, 285 K.

With the optimized reaction parameters, we investigated the generality of the catalytic reactions over Pd/CN. In some cases, slight adjustment of the reaction conditions was required due to the distinct reactivity of reactants. As shown in Table 2, a variety of unsaturated carbon-carbon bonds were successfully hydrogenated in good yields. The transfer hydrogenation of unsaturated C=C bonds was successfully achieved even in the presence of reducible substituents, such as carbonyl and ester group (Table 2, entry 10-11). Both isolated olefins and conjugated olefins afforded the

corresponding alkanes in good yield (entry 1-9). Besides olefins, cycloalkenes were also studied (entry 8-9) with moderate to high conversions and excellent selectivity. It is mentionable that cis-1, 2-diphenylethylene (entry 13) has no reactivity even under more harsh condition presumably due to its steric effect, whilst transfer hydrogenation of trans-1,2-diphenylethylene proceeded smoothly with very high selectivity under standard conditions (entry 12). As shown in Table 2, among mono-substituted styrene (entry 2-4), the involvement of fluorine substitution decreases the electron density of

C=C bonds, thus increasing the time for complete conversion. Moreover, para-fluorostyrene was more active than meta-fluorostyrene and ortho-fluorostyrene, which is in accordance with positioning regularity of benzene ring.

It is worth noting that transfer hydrogenation of α,β-unsaturated ketone, exemplified by chalcone here (entry 10, Table 2), were also achieved over the dyadic catalyst at room temperature in water with very high selectivity and good conversion. Such a high conversion is comparable with that over bench-mark homogeneous catalysts.[17] Cinnamic acid benzyl ester (Table 2, entry 11) gave a relatively low yield (21%) of target product due to the fracture of ester group according to GC-MS analysis (Figure S15). Further investigations on the asymmetric reactions of α, β-unsaturated ketones are in progress. Nevertheless, the function group tolerance and the high chemoselectivity of metal/CN dyadic catalysts have already been demonstrated here.

Conclusions

In conclusion, we investigated the possibility of significantly promoting the activity of metal NPs by using Mott-Schottky catalyst for transfer hydrogenation of unsaturated carbon-carbon bonds. FA was used as liquid hydrogen resource. This work is the first example of heterogeneous catalyst for chemoselective transfer hydrogenation of unsaturated organic compounds to saturated ones in water at room temperature. Fast separation of oil phase from the aqueous catalytic media combined with the high stability of the Pd/CN catalysts and low cost and toxicity of hydrogen source FA renders the catalytic system rather suitable for industrial applications. Further engineering the interface and electronic structure of metal-NPs/CN dyads should generate new possibilities to develop more efficient and sustainable catalysts for biofuel and green catalytic system. Effort is also being devoted to finding non-precious metal-based nanoparticles to construct Mott-Schottky catalyst for sustainable organic synthesis in our lab

Notes and references

L. H. Gong, Y. Y. Cai, Prof. X. H. Li, Y. N. Zhang, Dr. J. Su, Prof. J. S. Chen

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai, 200240, (People's Republic of China)

Fax: (+86)-21-5474-1297

E-mail: xinhaoli@sjtu.edu.cn (XHL), chemcj@sjtu.edu.cn (JSC)

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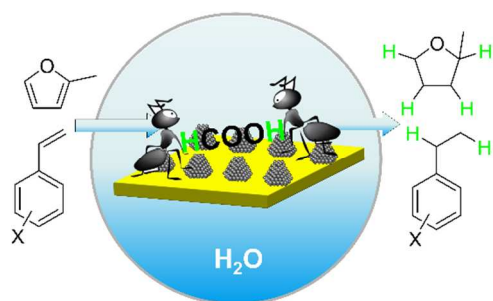
Transfer hydrogenation of unsaturated compounds can be conducted over Pd/CN catalysts at room-temperature in an aqueous solution of formic Acid.