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Volume 12 | Number 9 | September 2010 | Pages 1481–1676

ISSN 1463-9262

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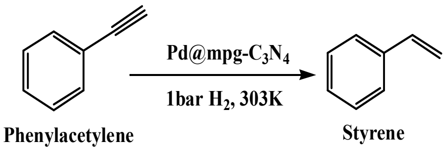

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DOI: 10.1039/C3GC40779A

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PAPER

Palladium nanoparticles supported on mpg-C_3N_4 as active catalyst for semihydrogenation of phenylacetylene under mild conditions

Dongshun Deng,*[a] Yang Yang[b], Yutong Gong[b], Yi Li[b], Xuan Xu[b] and Yong Wang*[b]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Palladium nanoparticles supported on a mesoporous graphitic carbon nitride, Pd@mpg-C_3N_4, has been developed as an effective, heterogeneous catalyst for the liquid phase semihydrogenation of phenylacetylene under mild conditions (303 K, atmospheric H_2). A total conversion was achieved with the high selectivity of styrene (higher than 94%) within 85 minutes. Moreover, the spent catalyst can be easily recovered by filtration and then reused nine times without apparent lose of selectivity. The generality of Pd@mpg-C_3N_4 catalyst for partial hydrogenation of the alkynes was also checked on terminal and internal alkynes with similar performance. The Pd@mpg-C_3N_4 catalyst was proven to be of industrial interesting.

Introduction

Semihydrogenation of phenylacetylene possesses considerable importance because phenylacetylene is regarded as a harmful component in feedstock for the industrial manufacture of polystyrene. It is mandatory to control the concentration of phenylacetylene below 10 ppm because the residual phenylacetylene will deactivate the polymerization catalyst and decrease the degree of polymerization.[1] Therefore it is desirable to develop new catalysts which can still maintain the high selectivity of styrene at phenylacetylene conversion near 100%.

For practical point of view, the hydrogenation process extensively utilizes the heterogeneous catalysts which are economically attractive for industrial applications due to their advantages of simple separation processes as well as good recycling properties. With the considerable attention on the liquid-phase hydrogenation of phenylacetylene, many heterogeneous catalysts have been reported. For example, Mastalir et al reported the use of Pd nanoparticles on hydrotalcite with selectivity around 90% at total conversion under mild reaction condition. [2] Their results are similar with those obtained by Guczi et al using pumice-supported Cu-Pd catalyst.[3] Tiengchad et al[4] investigated phenylacetylene hydrogenation using Pd/SBA-15, and a 85% of selectivity of styrene was obtained at the complete conversion of phenylacetylene, which was attributed to the geometrical confinement effect of the support. The similar effect was also illustrated in the Pd nanoparticles encapsulated in the MCM-41 supports via simultaneous synthesis method with a 96% selectivity of styrene. [5] The presence of strong metal-support interaction in Pd /SiO_2 could enhance the styrene selectivity to 86-90% near the 100% conversion of phenylacetylene.[6] Cazorla-Amorós et al. compared catalysts with different carbon supporting materials, including multiwall carbon nanotubes, black carbon and activated carbon.[1b] Their results suggested that Pd/NTs was a stable catalyst in performance with high selectivity of 95% after 5 cycles. Cazorla-Amorós et al. also prepared metallic nanoparticles with different compositions, mainly including Ni-Pd, Fe-Pd, Mg-Pd, Pd and Pt. Under 1 bar of H_2 and 323 K, these catalysts provided high selectivity and activity.[7] Oligomeric aramides were also used as support for palladium, the catalytic performance was relative low, especially in the region of 100% conversion of phenylacetylene. [8] The somewhat similar behavior was observed with the Pd/carbon.[9] Kaneda et al. applied Pd/SiO_2-DMSO catalyst system for this reaction, and selectivity of 100% at conversion of 98% was obtained under 1 bar of H_2 and 303 K.[10]

In the construction of heterogeneous catalysts for semihydrogenation of phenylacetylene, it is evident that palladium was basically chosen as catalytic center because of its specific dissociation power for hydrogen gas.[11] The choice of support is vital because the interaction between metal and active phase plays crucial role in the comprehensive performance of the catalysts. It is well known that the alkyne is relatively easy to be hydrogenated to form olefin, but the deep hydrogenation is inescapable.[12] Therefore how to improve the selectivity, especially persist high selectivity of olefin near the complete conversion of alkyne, is still a challenging. One method usually used is the addition of various modifiers such as metal[13] or organic base[14]. Another effective way is the selection of suitable support with special properties to modify the metal nanoparticles, including dispersion capability, stability and electron effect. Mesoporous graphic carbon nitrides are new emerging dotted carbon materials and possess suitable surface areas, small particles size, tunable pore diameter, extreme chemical and thermal stability, interesting electrical and semiconducting properties.[15] They have the potentiality to modify the central palladium metal and can be used as support material for heterogenous catalyst. In our previous work[16], taking the advantage of lewis base of nitrogen functionalities on the surface of mpg-C_3N_4, Pd@mpg-C_3N_4 was successfully prepared and used for selective hydrogenation of phenol and nitrile with perfect performance. Despite many efforts devoted to the study of heterogeneous hydrogenation of phenylacetylene, no example using doped carbon as supports can be found in the literature. In this paper, we hope to extend the Pd@mpg-C_3N_4 to the present semihydrogenation reaction. The electron-donation effect of mpg-C_3N_4 can increase the density of the anchored palladium. In turn, increasing electron density of palladium leads to favoring desorption of the monoenes to give a high yield of partially hydrogenated styrene. [17] An increase in alkene selectivity by addition of electron donor compounds such as ammonia or piperidine to supported palladium catalysts has been reported by Del Angel and Boitiaux.[18]

Result and discussion

Catalyst characterization

The obtained mpg-C_3N_4 material and supported Pd@mpg-C_3N_4 catalysts were systematically characterized using serials parameters, including BET surface area and pore volume, TEM, WAXS, FT-IR, and XPS, with the results illustrated in our previous work.[16] The supported Pd particles were well-dispersed and existed mainly as Pd^0 on the surface of the catalyst (~70%). The π-bonded planar C-N-C-layers along with incompletely condensed amino groups in mpg-C_3N_4 are suitable for stabilizing highly dispersed Pd^0 particles and prevent their re-oxidation. Such characters were helpful for the selective semihydrogenation of phenylacetylene. It needed to specify here is that the surface areas and average pore diameters of Pd@mpg-C_3N_4 samples decreased a little compared with those of the mpg-C_3N_4, which illustrated the metal potions attached to the surface of the pores in the support. This process made the pore diameters decrease, but the structures of the pore unchanged. The ICP-AES was used to determine the practical palladium contents in the prepared Pd@mpg-C_3N_4 catalysts, the experimental results are basically consistent with the desired compositions (as shown in table 1). The results demonstrated that the ultrasonic-assisted impregnation method was a simple and feasible way to control the palladium contents on the support of mpg-C_3N_4.

Table 1 Practical palladium content in the Pd@mpg-C_3N_4 catalysts.

Entry	Catalysts	ICP-AES results
1	1%Pd@mpg-C_3N_4	0.67%
2	4%Pd@mpg-C_3N_4	3.56%
3	6%Pd@mpg-C_3N_4	5.64%
4	12%Pd@mpg-C_3N_4	11.30%

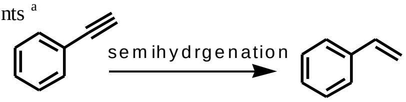
Semihydrogenation of phenylacetylene

The ideal destination of the semihydrogenation of phenylacetylene is the single reduction of carbon-carbon triple bond to form styrene. However, the deep reduction involving the formation of ethyl benzene is inevitable and will decrease the selectivity of styrene. Therefore, it is desirable to minimize the side reaction by utilizing the new catalyst with excellent performances.

The effect of solvent

Solvents are often used in heterogenous catalytic hydrogenation reactions. Solvents may be one of the best means available for markedly altering the rate as well as selectivity, a fact not sufficiently appreciated. So, the initial attempt was performed to investigate the influence of different solvents on the reaction. The corresponding conversion and selectivity are summarized in Table 2, along with the properties of the used solvents. Although the mechanistic basis of the solvent influences on the heterogeneous hydrogenation is not clear, some conclusions have been rationalized by correlating the reaction rate and selectivity with H_2 solubility or polarity. However, in present system, no systematic correlation can be discerned between the catalytic performance of Pd@mpg-C_3N_4 and H_2 solubility or solvent polarity. This phenomenon is also observed in the chemselective hydrogenation of quinoline using Pd@ompg-C_3N_4 [20] and the earlier study on the same system. [2] Among the organic solvents tested, tetrahydrofuran gave high activity but relative lower selectivity toward styrene. Ethanol was found to be the most effective, which gave both high conversion and selectivity relatively. Other solvents demonstrated low activity. In fact, because of the hydrophilcity of the nitrogen doped carbon support, the catalyst pd@mpg-C_3N_4 couldn't be dispersed well even with vigorous stirring in the non-polar and less polar solvents, which might produce unfavorable influence on mass transfer process. It is well known that ethanol is a cheap and versatile medium and its relative low boil point can simplify the separation process for the products. According, we selected ethanol as the reaction medium in the subsequent research. Furthermore, the amount of ethanol was also optimized, with the results listed in Table 3. It is evident that the amounts of ethanol made significant effect on the reaction rate but less influence on the selectivity. The concentration of phenylacetylene in entry 1 was almost 5 times higher than that in entry 5, but the reaction rate was much lower, which is very interesting. This result illustrated that the reaction rate had nothing to do with the concentration of phenylacetylene in the system, which suggested this reaction probably was a zero order reaction.[21] On the basis of the saturation concentration of H_2, the low concentration of phenylacetylene and high reaction rate suggested that the absorption and activation of H_2 may be the rate controlling step in the reaction kinetics.

Table2 Semihydrogenation of phenylacetylene with Pd@mpg-C_3N_4 in various solvents [a]



Entry	Solvents	Conv. [b] (%)	Sel. [b] (%)	δ [c]	p [d]
1	n-hexane	24	81	4.70	0.06
2	cyclohexane	39	96	3.97	0.10
3	toluene	58	96	3.40	2.40
4	tetrahydrofuran	93	89	3.50	4.20
5	ethyl acetate	44	96	3.77	4.30
6	chloroform	10	97	--	4.40
7	dioxane	45	95	1.90	4.80
8	ethanol	62	96	2.90	4.30

[a] Reaction conditions: 5.85 mmol phenylacetylene, 10 mg Pd@mpg-C_3N_4 (5.64wt% Pd), 303 K, 50 cm^3 solvent, atmospheric H_2 balloon, 60 minutes. [b]Analysed by GC and GC-MS . [c]Solubility of H_2 (10^6 $mol.cm^{-3}$, taken from Ref.(2, 21). [d] Solvent polarity.

Table 3 Hydrogenation of phenylacetylene with different amounts of ethanol [a]

Entry	Amount (cm^3)	Conv. [b] (%)	Sel. [b] (%)
1	10	20	97
2	20	49	96
3	30	57	96
4	40	59	96
5	50	62	96

[a] Reaction conditions: 5.85 mmol phenylacetylene, 10 mg Pd@mpg-C_3N_4 (5.64wt% Pd), 303 K, atmospheric H_2 balloon, 60 minute. [b] Analysed by GC.

The comparison of various catalysts

In order to investigate the detailed catalytic performance of the Pd@mpg-C_3N_4, we compared the catalytic hydrogenation results obtained under the same reaction conditions by using Pd@mpg-C_3N_4 and several other heterogeneous catalysts, including Lindlar catalyst, commercially available Pd@carbon, as well as several inorganic oxide supported catalysts of Pd@TiO_2, Pd@MgO, Pd@γ-Al_2O_3, and Pd@CeO_2, with the results listed in Table 4.

Table 4 Hydrogenation of phenylacetylene catalyzed by various catalysts[a]

Entry	Catalyst	Time/min	Conv. [b] (%)	Sel. [b] (%)
1[c]	Pd@carbon	15	85	88
2[d]	Pd@mpg-C_3N_4	85	>99	94
3[d]	2.5Au-Pd@mpg-C_3N_4	60	29	96
4[d]	Pd@γ-Al_2O_3	45	>99	90
5[e]	Pd@TiO_2	20	100	86-90
6[d]	Pd@MgO	105	>99	91
7[d]	Pd@CeO_2	150	95	91
8[f]	Lindlar catalyst	270	5	>99
9[g]	Pd@mpg-C_3N_4	60	17	97

[a] Reaction conditions: 10 mg catalyst, 5.85 mmol phenylacetylene, 50 cm^3 ethanol, 303 K, atmospheric H_2 bubbling. [b] Analysed by GC. [c] Data taken from ref 9, 1 wt% Pd, 0.2 MPa H_2 and 323 K. [d] 5.64 wt% Pd. [e] Data taken from ref 6b,1 wt% Pd, 5 bar H_2 and 303K. [f] 1 wt% Pd , provided by NHU company. [g] 0.67 wt% Pd.

In general, all the catalysts demonstrated high selectivity of styrene but evidently different activity in the semihydrogenation of phenylacetylene. Carbon material was extensively used as support in this reaction[22], when commercial Pd@carbon was used as catalyst, the results demonstrated that high selectivity of 88% was maintained up to conversion of 85% (Table 4, entry 1), while the selectivity decreased markedly with the further consumption of substrate. If replaced the support with multiwall carbon nanotubes, the selectivity was still better than 95% after five recycles because of the geometrical confinement effect.[7]

The inorganic oxide supported palladium catalysts were relatively effective for this reaction, while affording lower selectivity of styrene than Pd@mpg-C_3N_4 (Table 4, entry 2, 4-6). The reasons may arise from the uneven distribution of active position of palladium on the inorganic oxide surface. On the same time, because of the strong correlation between palladium and the metal oxides, it isn't easy to recover the expensive Pd from the used catalysts with low activity, which would increase the total cost without doubt.

It is well acknowledged that Lindlar catalyst is widespread-used in semihydrogenation of acetylene. Under the same reaction condition, the catalytic performance of Lindlar catalyst was compared with Pd@mpg-C_3N_4 (Table 4, entry 8, 9), the former gave nearly 100% selectivity but low conversion. The catalytic activity of Pd@mpg-C_3N_4 is 15 times faster than that of Lindlar catalyst, while keeping the high selectivity of 97%.

It is evident that the nature of the support materials plays a vital role in the performance of the palladium for present reaction. The mpg-C_3N_4 possesses the advantages of specific surface areas and electron density, which benefit the interaction of palladium with support, the morphorlogy and distribution of the palladium ion, and desorption of styrene. The comprehensive effects may be decisive for the satisfactory selectivity.

It was reported that the addition of second metal would enhance the selectivity,[13] so we prepared and applied Au-Pd@mpg-C_3N_4 with the molar ration of Au with Pd at 2.5 in the reaction, but the catalytic activity was much lower than that of Pd@mpg-C_3N_4.

Comparing the results obtained by using various catalysts, it was indicated that the Pd@mpg-C_3N_4 provided both high conversion and selectivity relatively, and because of its convenient preparation method and good characteristics of the mesoporous graphitic carbon nitride (mpg-C_3N_4), it was easier to get catalyst with distributed active portion on the surface, which made a steady catalytic activity. Furthermore, when the catalyst was lost activity completely, it is easy to recycle the expensive palladium by a simple burning process.

Kinetic analysis and reusability studies of Pd@mpg-C_3N_4 catalyst on semihydrogenation of phenylacetylene

For heterogeneous catalytic hydrogenation reaction, it is necessary to eliminate the influences of mass transfer limitations on the hydrogenation activity and selectivity of the catalyst. On the basis of previous experiments performed with different stirring rates and hydrogen flows, we carried out the experiments using phenylacetylene (5.85 mmol), ethanol (50 cm^3), 303 K, H_2 (atmospheric flow, 30 $cm^3.min^{-1}$) and magnetic stirring (1500 rpm) under different weights of catalysts (2-12mg). The evolution of material was monitored with reaction time. As illustrated in the literature[9, 23], the reaction can be regarded to follow zero order kinetics with respect to concentration of phenylacetylene. So, the apparent rate (*k*) can be obtained from the slope by linear fitting of concentration of phenylacetylene *vs*. time. The apparent reaction rates are measured for applying the Koros-Nowak criterion[24], and the results are illustrated in Figure 1. As can be seen, the apparent reaction rate is proportional to the amount of catalyst. It is proven that the performance of catalyst under the experimental conditions is within the kinetic regime and the reaction is free of artifacts.

In the following reutilization studies of Pd@mpg-C_3N_4 for semihydrogenation of phenylacetylene, the reaction scale was enlarged. 29.25 mmols of Phenylacetylene and 50 mg of catalyst were stirred in 150 cm^3 of ethanol at 303 K under atmospheric H_2 flow of 30 cm^3min^{-1}. When the conversion of phenylacetylene arrived at about 90%, the reaction was terminated. The catalyst was separated from the reaction mixture by simple centrifugation, and then was thoroughly washed with ethanol and dried at 343 K. This catalyst was used for another eight reaction cycles. The reaction course was monitored with time for every cycle to evaluate the performance of the catalyst. For best illustration, the conversions of phenylacetylene vs time for several cycles were plotted in Figure 2. Using the method mentioned above, the apparent reaction rate for each cycle can be determined and listed in Table 5, along with the ultima conversion and selectivity. Actually, the reaction rate decrease gradually with the recycling

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runs. For the heterogeneous catalysis, metal species leaching during the recycle reaction is one problem. Palladium content of the used catalyst after nine recycles was 2.18 wt% by ICP-AES analysis, which demonstrated that the gradually decreased activity of the Pd@mpg-C_3N_4 was primarily due to progressive palladium leaching during the separation and purification operation.

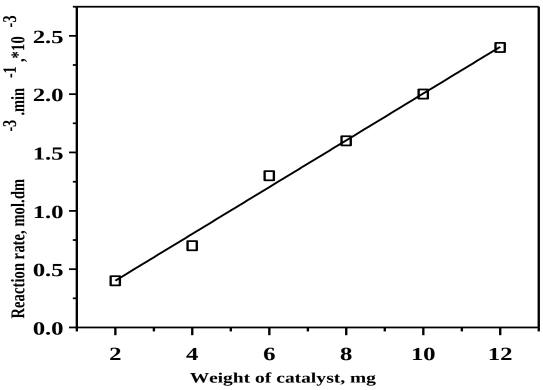


Fig. 1 The reaction rate *vs* weight of catalyst

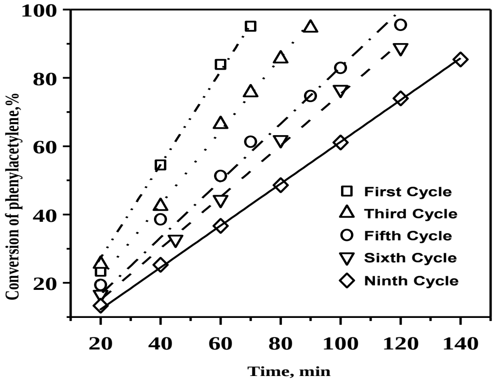


Fig. 2 The conversion of phenylacetylene *vs* time

Table 5 Reusability studies of Pd@mpg-C_3N_4 catalyst[a]

Reaction cycle	1st	2nd	3rd	4th	5th	6th	7th	8th	9th
Reaction time (min)	70	70	90	100	120	120	140	160	140
Conversion of phenylacetylene (%)	95	91	95	93	96	89	95	98	85
Selectivity of styrene (%)	95	94	94	95	94	95	94	93	96
k_{app} (mol.dm^{-3}min^{-1})	1.37	1.29	1.07	0.93	0.83	0.75	0.68	0.63	0.61

[a] Reaction conditions: phenyacetylene 29.25 mmol, Pd@mpg-C_3N_4(5.64 wt% Pd, recovered) 50 mg, ethanol 150 cm^3, 303 K, H_2 (atmospheric, 30 cm^3.min^{-1}).

Possible reaction pathway and mechanism for the semihydrogenation of the phenylacetylene

As the Pd@mpg-C_3N_4 demonstrated excellent performance in the present reaction, more studies were applied for further understand of the catalytic process. The plot of phenylacetylene conversion and product selectivity versus reaction time was shown in Figure 3. The reaction was fast and styrene was obtained as the predominant product (96% in selectivity) until the conversion reached 90%, and then styrene slowly transferred to ethyl benzene but the selectivity was still above 94% at the total conversion of phenylacetylene after reaction for 85 minutes. The mechanism and kinetic model for the phenylacetylene hydrogenation have been investigated in the literatures.[23b, 23c, 25]

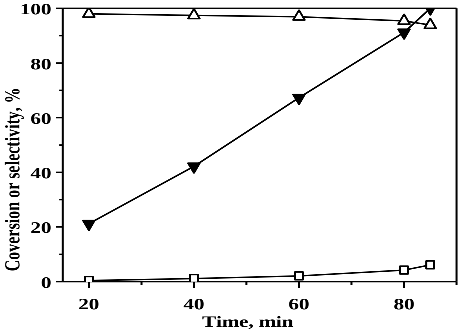
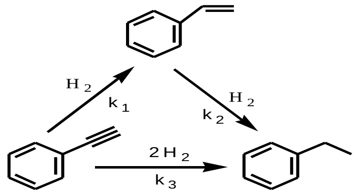


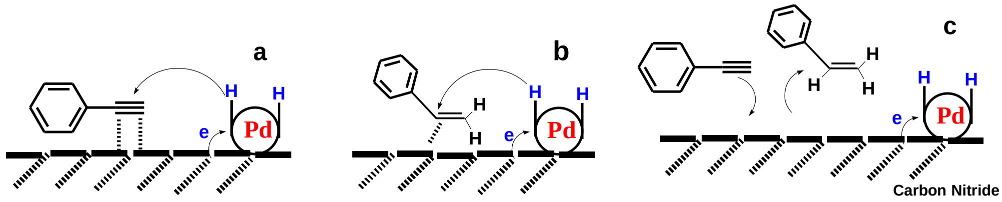
Fig.3 Variation of conversion and selectivity with reaction time on the semihydrogenation of phenylacetylene. Reaction conditions: 10 mg 5.64 wt% Pd@mpg-C_3N_4, 5.85 mmol phenylacetylene, 50 cm^3 ethanol, 303 K, atmospheric H_2 bubbling. (▼) Conversion of phenylacetylene and selectivity to styrene (△) or ethyl benzene (□).

As depicted in Schem 1, the hydrogenation of phenylacetylene to styrene or ethyl benzene is considered to occur by two-pathway mechanism. The first pathway involves the completely hydrogenation of triple bond to saturated single bond, while another pathway is the successive hydrogenation reactions involving styrene as the intermediate. Therefore, in order to improve the selectivity of styrene, the further hydrogenation of styrene and direct hydrogenation of phenylacetylene must be minimized. Applying density function theory in simulations of selective hydrogenation using Lindlar catalyst, M. García-Mota et al.[26] proposed that the heterogenous catalyst with the high selectivity should possess three positive contributions including high thermodynamic factor, no generation of β-PdH phase, and no promotion for formation of oligomerization. As for Pd@mpg-C_3N_4[16], its surface is electron negative. The HRTEM images revealed well-dispersed Pd particles with a mean size of 3.3 nm, which is helpful to decrease the formation of the palladium β-hydride phase.[27] The lewis base moisture in the mpg-C_3N_4 is able to increase the electron density of palladium, in turn, leads to decreasing the strength of adsorption of intermediate styrene. Desorption of styrene is favored and the overall selectivity is enhanced. This is consistent with the reported result.[17] As reported in a recent paper[28], the nitrogen base can promote the formation of $Pd^{\delta+}$-$H^{\delta-}$ in the polarization of Pd-H bond, which prefer to attack the triple bond.



Scheme 1 The pathway for the semihydrogenation of phenylacetylene.

Schem 2 illustrates the hydrogenation process of the phenylacetylene. In the initial step, phenylacetylene was absorbed on two catalyst sites as earlier research suggested [23b] and and H_2 is dissociated by the electronically supported Pd (Schem 2a). The triple bond is converted to double bond by the attack of the activated hydrogen atom (Schem 2b). Another activated hydrogen inserts and the formed styrene is rejected from the support, being replaced by a new phenylacetylene molecular (Schem 2c).

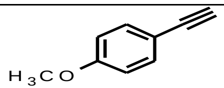
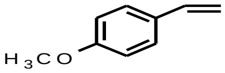
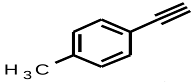
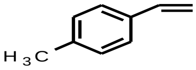
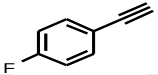
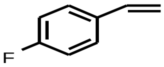
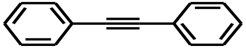
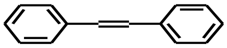


Scheme 2 Proposed reaction mechanism for semihydrogenation of phenylacetylene catalyzed over Pd@mpg-C_3N_4

Catalytic performance of Pd@mpg-C_3N_4 for the semihydrogenation of various alkynes

To explore the scope of the Pd@mpg-C_3N_4 catalytic system for the partial reduction of alkynes to alkyene, a serial of alkynes with structurally divergent functional groups or triple bond position were examined, with the results listed in Table 6. The catalytic system was effective for aromatic alkyene regardless of the benzene ring substituted by electron-donating or electron-withdrawing group (Table 6, entry 1-3). The catalyst demonstrated excellent activity and selectivity for the semihygrogenation of various terminal alkynes as well as internal alkynes (Table 6, entry 4-6), which is of great importance. But it should be noted that the hydrogenation of aliphatic alkyene existed double bond isomer products (Table 6, entry 5, 6). Unlike some catalysts are just able to catalyze one kind of alkynes, the results show that the Pd@mpg-C_3N_4 is extensively capable of semihydrogenation for different kinds of alkynes with high selectivity.

Table 6 Semihydrogenation of various alkynes catalyzed by Pd@mpg-C_3N_4 catalyst[a]

Entry	Substrate	Product	Time (min)	Conv. [b] (%)	Sel.[b] (%)
1			150	38	94
2			90	>99	94
3			30	99	93
4			60	>99	72
5[c]	1-Octyne	1-Octene and isomer alkenes	80	>99	93
6[c]	4-Octyne	4-Octene and isomer alkenes	20	>99	99

[a] Reaction conditions: 10 mg 5.64 wt% Pd@mpg-C_3N_4, 5.85 mmol substrate, 50 cm^3 ethanol, 303K, atmospheric H_2 balloon. [b]Determined by GC using an internal standard. [c]Determined by GC-MS, including double bond isomer products.

Experimental

Materials and analytical methods

Unless specific stated, all the chemicals were analytical grade and commercially purchased from Sigma–Aldrich, Acros, Merck, or Aladdin chemical reagents Co. Ltd. (Shanghai, China). The chemicals were used without further purification as received. The conversion and selectivity of the reaction were determined by chromatographic analysis using SHIMADZU GC-2011 with FID detector.

Preparation of catalysts

The support material of mpg-C_3N_4 and heterogenous catalysts Pd@mpg-C_3N_4 were prepared according to our reported method.[16] The inorganic oxides supported palladium catalysts were obtained according to literature.[19]

Typical procedure for semihydrogenation of phenylacetylene

Liquid-phase selective hydrogenation of phenylacetylene was carried out in a 100 cm^3 round-bottled flask. In a typical procedure, 10 mg Pd@mpg-C_3N_4, 5.85 mmol phenylacetylene and 50 cm^3 ethanol were placed in the vessel. After the replacement of air with H_2 for 3 times, the mixture was then magnetically stirred at 1500 rpm under atmospheric hydrogen ball and 303 K. The reaction process was monitored by gas chromatographic analysis.

Conclusions

In summary, as a heterogeneous catalyst, the Pd@mpg-C_3N_4 demonstrated considerable catalytic activity in the

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DOI: 10.1039/C3GC40779A

semihydrogenation of phenylacetylene at mild conditions (303 K, atmospheric H_2). Especially, the Pd@mpg-C_3N_4 demonstrated quite stable performance in the recycling tests, which is proven as a novel, effective, and environment-friendly catalyst. Our experimental results also show that the Pd@mpg-C_3N_4 is widely applicable for different kinds of alkynes with quite high conversion and selectivity.

Acknowledgements

Financial support from the Joint Petroleum and Petrochemical Funds of the National Natural Science Foundation of China and China National Petroleum Corporation (U1162124), the Zhejiang Provincial Natural Science Foundation for Distinguished Young Scholars of China (LR13B030001), the Specialized Research Fund for the Doctoral Program of Higher Education (J20130060), the Fundamental Research Funds for the Central Universities, the Program for Zhejiang Leading Team of S&T Innovation, and the Partner Group Program of the Zhejiang University and the Max-Planck Society are greatly appreciated.

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References

1 (a) B. R. Maurer and M. Galobardes, US Patent 4,822,936, 1989;
(b) S. Domínguez-Domínguez, Á. Berenguer-Murcia, B. K. Pradhan, A. Linares-Solano and D. Cazorla-Amoros, *J. Phys. Chem. C*, 2008, **112**, 3827.
(c) K. H. Lee, B. Lee, K. R. Lee, M. H. Yi and N. H. Hur, *Chem. Commun.*, 2012, **48**, 4414.
2 Á. Mastalir and Z. Király, *J. Catal.*, 2003, **220**, 372.
3 L. Guczi, Z. Schay, Gy. Stefler, L. F. Liotta, G. Deganello and A. M. Venezia, *J. Catal.*, 1999, **182**, 456.
4 N. Tiengchad, O. Mekasuwandumrong, C. N. Chiangmai, P. Weerachawanasak and J. Panpranot, *Catalysis Communications*, 2011, **12**, 910.
5 S. Domínguez-Domínguez, Á. Berenguer-Murcia, Á. Linares-Solano and D. Cazorla-Amorós, *J. Catal.*, 2008, **257**, 87.
6 (a) P. Weerachawanasak, P. Praserthdam, M. Arai and J. Panpranot, *J. Mol. Catalysis A: Chem.*, 2008, **279**, 133;
(b) P. Weerachawanasak, O. Mekasuwandumrong, M. Arai, S. I. Fujita, P. Praserthdam and J. Panpranot, *J. Catal.*, 2009, **262**, 199.
7 S. Domínguez-Domínguez, Á. Berenguer-Murcia, D. Cazorla-Amoros and A. Linares-Solano, *J. Catal.*, 2006, **243**, 74.
8 F. Arena, G. Cum, R. Gallo and A. Parmaliana, *J. Mol.Catal. A: Chem.*, 1996, **110**, 235.
9 S. D. Jackson and L. A. Shaw, *Applied Catalysis A: General*, 1996, **134**, 91.
10 Y. Takahashi, N. Hashimoto, T. Hara, S.Shimazu, T. Mitsudome, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Chem. Lett.* 2011, **40**, 405.
11 M. Y. Ni and Z. Zeng, *J. Mol. Struct.: THEOCHEM*, 2009, **910**, 14.
12 P. N. Rylander, *Hydrogenation Methods*, Academic Press, London, New York, 1985.
13 H. Lindlar and R. Dubuis, *Org. Synth.*, 1966, **46**, 89.
14 A. S. Kende, P. Fludzinski, J. H. Hill, W. Swenson and J. Clardy, *J. Am. Chem. Soc.*, 1984, **106**, 3553.
15 (a) A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J. O. Muller, R. Schlogl and J. M. Carlsson, *J. Mater. Chem.*, 2008, **18**, 4893;
(b) J. S. Lee, X. Wang, H. Luo and S. Dai, *Adv. Mater.*, 2010, **22**, 1004.
16 (a)Y. Wang, J. Yao, H. R. Li, D. S. Su and M. Antonietti, *J. Am. Chem. Soc.*, 2011, **133**, 2362;
(b)Y. Li, X. Xu, P.F. Zhang, Y. T. Gong, H. R. Li and Y. Wang, *RSC Advance*, Dio: 10.1039/c3ra41397g;
(c)Y. Li, Y. T. Gong, X. Xu, P. f. Zhang, H. R. Li and Y. Wang, *Catal. Commun.*, 2012, **28**, 9.
17 Z. M. Michalska, B. Ostaszewski, J. Zientarska and J. W. Sobczak, *J. Mol. Catal. A: Chem.*, 1998, **129**, 207.
18 (a) G. Del Angel, J.L. Benitez, *J. Mol. Catal.*, 1994, **94**, 409;
(b) J. P. Boitiaux, J. Cosyns, S. Vasudevan, *Appl. Catal.*, 1985, **15**, 317.
19 X. Xu, Y. Li, Y. T. Gong, P. F. Zhang, H. R. Li and Y. Wang, *J. Am. Chem. Soc.*, 2012, **134**, 16987.
20 Y. T. Gong, P. F. Zhang, X. Xu, Y. Li, H. R. Li and Y. Wang, *J. Catal.*, 2013, **297**, 272.
21 U. K. Singh and M. A. Vannice, *Applied Catalysis A: General*, 2001, **213**, 1.
22 R. A. Sheldon and H. V. Bekkum, *Fine Chemicals Through Heterogeneous Catalysis*, Wiley-VCH, 2001.
23 (a) B. M. Choudary, K. M. Lakshmi, R. N. Mahender, R. K. Koteswara, Y. Haritha, V. Bhaskar, F. Figueras and A. Tuel, *Appl. Catal. A General*, 1999, **181**, 139;
(b) D. Duca, L. F. Liotta and G. Deganello, *J. Catal.*, 1995, **154**, 69;
(c) N. Martín-Astorga, G. Pecchi, T. J. Pinnavaia, G. Alvez-Manoli and P. Reyes, *J. Mol. Catal. A: Chem.*, 2006, **247**, 145;
(d) B. A. Wilhite, M. J. McCready and A. Varma, *Ind. Eng. Chem. Res.*, 2002, **41**, 3345.
24 R. J. Madon and M. Boudart, *Ind. Eng. Chem. Fundam.* 1982, **21**, 438.
25 Á. Molnár, A. Sárkány and M. Varga, *J. Mol. Catal. A: Chem.*, 2001, **173**, 185.
26 M. García-Mota, J. Gómez-Díaz, G. Novell-Leruth, C. Vargas-Fuentes, L. Bellarosa, B. Bridier, J. Pérez-Ramírez and N. López, *Theor. Chem. Acc.*, 2011, **128**, 663.
27 G. Carturan, G. Facchin, G. Cocco, S. Enzo and G. Navazio, *J. Catal.*, 1982, **76**, 405.
28 J. Yu and J.B. Spencer, *Chem. Commun.*, 1998, 1103.