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Graphene-supported Pd nanoparticles: microwave-assisted synthesis and as microwave-active selective hydrogenation catalysts†

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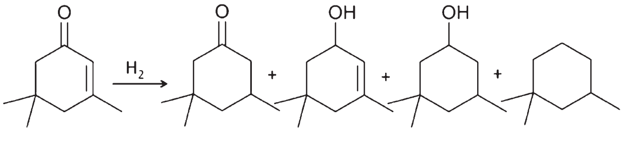
Facile synthesis of graphene-supported Pd nanoparticles (NPs) with an average size of 5 nm (Pd/G) was achieved by a microwave-assisted reduction approach; the obtained Pd/G can be very effectively coupled to the microwave field, making it a high-performance catalyst (with turnover frequency (TOF) of 158 465 h^{-1}) for microwave-assisted selective hydrogenation of isophorone at low temperatures.

Dihydroisophorone (3,3,5-trimethylcyclohexanone, DHIPO) is a solvent used for vinyl resins, varnishes, lacquers, paints and other applications, and can be produced through the selective hydrogenation of isophorone (3, 5, 5-trimethyl-2-cyclohexen-1-one) as shown in Scheme 1. In addition to nickel and nickel alloys,[1–3] Pd/C is the most commonly used catalyst for this reaction.[4–7] However, it is difficult to get a good selectivity at the same time as obtaining good activity in such a system.[8] While the boiling point of DHIPO (462 K) is close to that of *trans*-3, 3, 5-trimethylcyclohexanol (467 K), a by-product, excellent selectivity to the designated product is particularly important to avoid the complicated and time-consuming product separation and purification processes. Therefore, the development of a green and efficient process with the high conversion and selectivity is the urgent need for this important hydrogenation reaction.[8] Indeed, there are attempts to develop new methodologies for this reaction. For instance, supercritical carbon dioxide has proven to be a suitable green solvent system which leads to high reaction rates and easy separation of solid catalysts and products. Hence a commercialization of the process was realized.[8–12] However, as the combination of high activity/selectivity is rarely reported, there are room for developing new catalytic systems and therefore further improving the reaction efficiency.

Graphene (G) is a huge open π-electron system with a unique electronic structure, which ignites diverse applications such as electronics, photovoltaics, batteries, supercapacitors and so on.[13–15] Very recently, it has been shown that graphene can be used as the catalyst or the advantageous carrier for the catalytic active components for oxidation, hydrogenation and carbon-carbon coupling reactions.[16–24] However, graphene/layered carbons are very sensitive to microwave irradiation. Herein, we demonstrate the potential of a graphene-type support in the microwave-assisted synthesis of metal/graphene nano-composites. Significantly, because of the good ability to adsorb microwave of the obtained Pd NPs/graphene nano-composites, it is microwave-active in the low temperature selective hydrogenation reaction, leading to superior catalytic performance as compared to the conventional counterparts.

Graphene oxide (GO) was prepared by exfoliating graphite with strong oxidizing agents. GO was reduced by hydrazine hydrate in ammonia solution to generate chemically converted graphene (CCG).[25] 250 mg CCG and 25 mg palladium acetate were mixed with 30 ml 0.1 M sodium dodecyl sulfate solution in 80 ml quartz tube. The mixture was sonicated at room temperature for 1 h. Microwave-assisted treatment of the mixture under 1.2 MPa hydrogen at 373 K for 30 min in a CEM Discover high pressure microwave apparatus. After filtration, washing and drying at 333 K for 12 h, Pd/G catalysts were obtained (Pd content of 3.2 wt.%, determined by ICP). The same method was applied for the synthesis of control catalysts, such as Pd/active carbon (Pd/AC), Pd/graphite (Pd/Grp) and Pd/SiO$_2$ (with Pd content of 3.7 wt.%, 5.0 wt.% and 4.4 wt.%, respectively, as determined by ICP) (Fig. S4, ESI†).



Scheme 1 The reaction of hydrogenation of isophorone.

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† Electronic supplementary information (ESI) available: synthesis, characterization, reaction conditions and other experimental details can be found in the ESI. See DOI: 10.1039/c3ra41340c

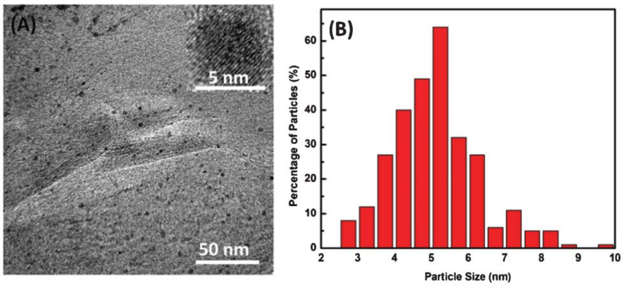


Fig. 1 TEM images (A) and size distribution (B) of Pd/G catalyst.

TEM images show that palladium nanoparticles with an average size of 5 nm were uniformly distributed over the carbon support (Fig. 1). The chemisorption experiments indicate that the metal dispersion is 18.8%, corresponding to the mean crystallite size of 5.9 nm, which agrees well with the TEM observation. As shown in O 1s XPS (Fig. S6, ESI†), the 532 eV and 533.5 eV is corresponding to C=O and C–O bond, respectively. There are more C–O species on active carbon but C=O species on graphite. Instead, graphene prepared by current method contains not only C–O species but also abundant C=O species. The synthesis process of Pd/G was followed by UV-vis spectroscopy. As shown in Fig. S1, ESI†, the peak corresponding to palladium acetate starts to decrease in 30 s under microwave irritation, indicating that the microwave-assisted reduction/nucleation processed very fast. After 1 min, it seems that the reduction process completed, demonstrating the efficiency of microwave-assisted method. Following the same method, Pd/active carbon (Pd/AC), Pd/graphite (Pd/Grp), and Pd/SiO_2 catalysts were prepared. The chemical states of those Pd-based catalysts were studied by XPS (Fig. 2A). Clearly, the Pd/AC catalyst was dominated with the metallic Pd, while a peak at 336.9 eV for Pd/SiO_2 sample suggests that there are strong interaction between Pd and silica, leading to the formation of Pd–Si bond or PdO.[26,27] The graphite and graphene supported Pd NPs catalysts exhibit a peak at 335.3 eV with a shoulder at around 337.6 eV. This result implies that the valence state of the Pd/Grp and Pd/G catalysts were a mixture of metallic Pd and Pd^{2+}.

Microwave-assisted hydrogenation of isophorone was conducted at 333 K in a quartz pressure vessel, with water as the solvent and hydrogen (1.2 MPa) as the reducing agent. In a blank experiment without using catalyst, the results showed that no noticeable activity was observed by GC over a 5 min run (Table 1, entry 1). When the pristine graphene was used as catalyst for the isophorone hydrogenation reaction, no activity was presented either (Table 1, entry 2). When the 0.1 wt.% Pd/G was used as catalyst, a 17.4% isophorone conversion and 54% selectivity towards the desired product were observed (Table 1, entry 3). The catalytic performance increased with higher Pd loading (Table 1, entry 4 and Fig. S10, ESI†). When Pd loading reached 3.2 wt.%, an unexpected high isophorone conversion of 99.8% was observed with selectivity to DHIPO dramatically increased to 97%, demonstrating the possibility of coexistence of high activity and high selectivity (Table 1, entry 5). Significantly, the reaction time is just 5 min while the amount of catalyst used was 2 mg. This observation clearly indicates that Pd/G catalyst can be effectively coupled with microwave field, leading to the fast and highly efficient selective hydrogenation of isophorone. As a control, GO with more oxygen-containing groups (Fig. S7, ESI†) supported Pd catalyst (Fig. S8, ESI†) shows a relatively poor catalytic performance (Table S1, ESI†). Even if 2 mg pure Pd nanoparticles (Fig. S9, ESI†) were used as catalysts, its activity is still lower than that of Pd/G catalysts. For Pd/G catalyzed reaction, even if we increase the amount of substrate in the reaction, the catalytic performance remains almost the same, showing the Pd/G catalyzed hydrogenation is highly microwave-active (Table 1, entry 6 and 10). Indeed, a remarkable turnover frequency (TOF) of 158 465 h^{-1} was recorded for the 3.2 wt% Pd/G catalyst, which surpassed the conventional catalysts. Although both the components of Pd/G nano-composite can adsorb microwave, the integrity of composite is pivotal for the construction of a successive microwave-active catalytic system. As shown in Table 1, the Pd/AC, Pd/Grp and Pd/SiO_2 catalysts exhibited activity in the selective hydrogenation of isophorone. However, the concomitant good activity/selectivity under microwave irradiation condition can only be achieved over Pd/G nanocomposite catalyst. It is worth noting that both graphene and graphite possesses a giant π-system, which may promote reactant/catalysts interaction (especially for reactant with a π-system as in the current study) at the same time of adsorbing microwave.[28,29] However, Pd/Grp and Pd/G have a huge difference in reaction performance, albeit Pd/Grp is much better than Pd/AC and Pd/SiO_2. A possible explanation is that as CCG was prepared from the reduction of graphene oxide, the edge was decorated with carboxyls and other oxygen-containing groups, which make the catalyst well dispersed in the multi-phase reaction mixture (with water as solvent, isophorone as the organic phase, and the catalyst as the solid phase, see Fig. 3 and Fig. S2, ESI†). Most possibly, the

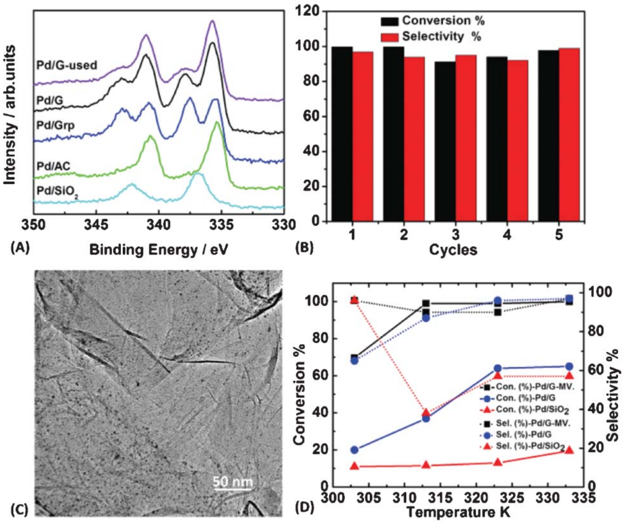


Fig. 2 The Pd 3d XPS spectra of different catalysts (A); The recycling of the Pd/G catalyst for the hydrogenation of isophorone (B) (1.2 MPa H_2, 333 K, 0.5 ml H_2O, 5 min, 2 mg 3.2 wt.% Pd/G, 3 mmol substrate, microwave-assisted); TEM images of used Pd/G catalyst (C); The effect of reaction temperature on catalytic behavior of different catalyst systems (1.2 MPa H_2, 0.5 ml H_2O, 0.5 mmol substrate, 5 min, 2 mg catalyst) (D).

Table 1 Microwave-assisted hydrogenation of isophorone under various conditions[a]

Entry	Catalysts	Loading amount (wt.%)	Time (min)	Conv. (%)	DHIPO Sel. (%)	TOF(/h)[d]
1	blank	—	5	—	—	—
2	graphene	—	5	—	—	—
3	Pd/G	0.1	5	17.4	54.1	290 236
4	Pd/G	0.6	5	29.2	85.5	85 363
5	Pd/G	3.2	5	99.8	97.4	52 818
6[b]	Pd/G	3.2	5	98.4	98.9	104 997
7	Pd/Grp	3.7	5	35.0	83.9	16 149
8	Pd/AC	5.0	5	9.0	>99.0	3073
9	Pd/SiO_2	4.4	5	7.4	>99.0	2871
10[c]	Pd/G	3.2	10	99.0	93.1	158 465

[a] Hydrogen pressure: 1.2 MPa, reaction temperature: 333 K, isophorone: 0.5 mmol, solvent: 0.5 ml H_2O, 2 mg catalyst, microwave-assisted reaction. [b] isophorone: 1 mmol. [c] isophorone: 3 mmol. [d] the metal dispersion was all unified regarded as 18.8%.

reaction occurred at the interfaces of various phases in the complicated reaction mixture while the good dispersion of the catalysts between the oil/water phases make itself very efficient in the adsorption/reaction. The application scope of this catalytic system was explored by using a variety of α, β-unsaturated ketone under similar reaction conditions. As summarized in Table 2, the Pd/G catalyst exhibited a good activity and selectivity for hydrogenation of all the reactants. Moreover, the catalytic performance of Pd/G catalyst remained at a very high level even after five reaction cycles, while there is no obvious particle aggregation observed after the reaction (Fig. 2B and C). This indicates clearly that Pd/G catalyst is a very stable catalyst for microwave-assisted hydrogenation reaction.

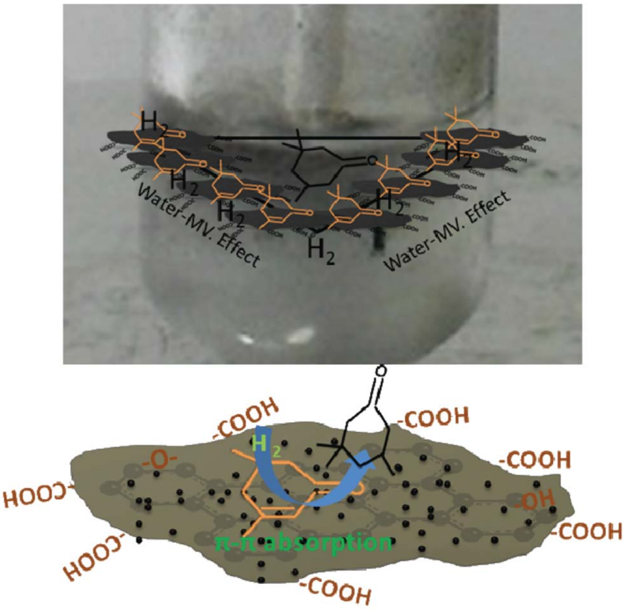
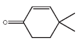
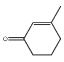
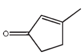
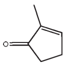
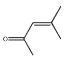


Fig. 3 Possible reaction scheme of microwave-assisted hydrogenation of isophorone: the edge of graphene was decorated with oxygen-containing groups which confers it surfactant-like capability, emulsifying the organic phase, isophorone, and water during the reaction. Moreover, water, especially graphene are able to couple with microwave field, making the transformation of the adsorbed α, β-unsaturated ketone very efficient.

In order to verify the function of microwave field in this reaction, the catalytic performance of these Pd/G and Pd/SiO_2 catalysts in microwave-assisted and conventional oil bath heating conditions was investigated in the hydrogenation of isophorone under different temperatures (Fig. 2D). Under conventional oil bath heating conditions at 303 K, the conversion of the reactions with Pd/G as catalyst was more than twice that of the Pd/SiO_2 (only 20%) while the selectivity was only about 70% of the latter. When the temperature was raised to 313 K, for Pd/SiO_2 it was surprising to observe that the selectivity dropped rapidly to about 40% while the conversion did not show a significant increase, which means raising temperature was beneficial to the formation of byproducts at this range. Further increase in the reaction temperature (through 323 K to 333 K), the conversion and selectivity improved modestly (Pd/SiO_2) with conversion less than 20% and selectivity about 60%. Instead, for Pd/G, only at a relatively high reaction temperature range (323 K to 333 K), a good conversion (60%) and selectivity (99%) was observed. This result reveals that in conventional oil bath heating conditions, Pd/SiO_2 was the catalyst with typical low conversion and higher selectivity at low

Table 2 Microwave-assisted hydrogenation of α, β-unsaturated ketone under the same conditions[a]

Entry	Substrate	Conversion (%)	Ketone Sel. (%)[b]	TOF(/h)[b]
1		98.0	93.8	52 285
2		97.1	99.6	51 751
3		83.7	98.6	44 282
4		99.1	99.6	52 818
5		>99.0	98.7	52 818

[a] 1.2 MPa H_2, 333 K, 0.5 ml H_2O, 5 min, 2 mg 3.2%Pd/G, microwave-assisted reaction. [b] the metal dispersion was 18.8%.

temperatures and low conversion with good selectivity at high temperatures. As for Pd/G catalyst under microwave irradiation, as Pd/G can be effectively coupled with microwave field from 303 K to 333 K, the catalytic performance is superior to those operated in the thermal heating mode. Therefore, from the above results, one can reach the conclusion that graphene is an excellent substrate for Pd nanoparticles and has a strong substrate-induced microwave-active effect for the catalytic reactions.

Conclusions

In conclusion, we have developed an efficient method to synthesize Pd/graphene nano-composite catalysts by microwave-induced hydrogen reduction method. The composite can be effectively coupled with microwave field, making it an excellent catalyst for selective hydrogenation reactions. In the microwave-assisted hydrogenation of isophorone reaction, an excellent catalytic behavior (with activity/selectivity higher than 95%, and a TOF of 158 465 h^{-1}) can be realized at ambient temperature in less than 5 min, surpassing its conventional counterparts operating both in thermal and microwave modes. Although the potential of this strategy is not yet fully demonstrated, it can already be seen to provide a simple, fast, and efficient approach for microwave-active graphene-based catalytic reactions.

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