## ChemComm

## COMMUNICATION

## **RSC**Publishing

View Article Online View Journal | View Issue

Cite this: Chem. Commun., 2013, 49, 2359

Received 8th November 2012, Accepted 6th January 2013

DOI: 10.1039/c3cc39011j

www.rsc.org/chemcomm

Reduction of alkenes catalyzed by copper nanoparticles supported on diamond nanoparticles<sup>†‡</sup>

Amarajothi Dhakshinamoorthy,\* Sergio Navalon, David Sempere, Mercedes Alvaro and Hermenegildo Garcia\*

Copper nanoparticles (Cu NPs) supported on diamond nanoparticles (D NPs) previously purified by Fenton treatment (Cu/D) followed by annealing with hydrogen (Cu/DH) are highly efficient and reusable heterogeneous catalysts for hydrogenation of styrene to ethylbenzene with the minimum productivity value of 30 617 cycles.

Reduction of olefins to saturated hydrocarbons is one of the fundamental transformations in organic chemistry which is usually performed using transition metal catalysts such as Pt, Pd, Rh and Ni and hydrogen as a reducing agent.<sup>1</sup> Although many catalysts are highly selective and active in hydrogenation reaction, the cost of these precious metals makes it convenient to look for other alternatives. Further, as an alternative to hydrogenation with H<sub>2</sub> gas, the use of hydrazine for reduction of olefins has attracted attention from both academia and industry.<sup>2–4</sup> This reagent has the advantage of avoiding the use of flammable gas and simplifies the reactor. It is generally accepted that double bonds are reduced by diimide, which is generated from hydrazine *via* oxidation.<sup>3</sup>

Reduction of olefins with hydrazine to the corresponding reduced products in high selectivity is performed using catalysts such as guanidine,<sup>5</sup> flavin derived catalysts<sup>6</sup> and metalorganic frameworks.<sup>7</sup> It has also been reported that metal nanoparticles (NPs) supported on suitable supports can also act as a selective catalyst in hydrogenation reaction.<sup>8</sup> For example,  $Fe_3O_4^{9}$  and Ni NPs supported on K10 clay<sup>10</sup> have been reported as catalysts for the hydrogenation of styrene to ethylbenzene using aqueous hydrazine as a reducing agent. Recently, we have reported that Au NPs supported on D NPs (Au/D) could be used as a catalyst for the degradation of phenol in the presence of hydrogen peroxide.<sup>11</sup> In continuation of our quest for using D NPs as a support (see Fig. S1, ESI‡ for TEM images) for the deposition of metal NPs, we have reported that Cu NPs supported on D NPs are selective catalysts for aerobic oxidation of thiophenol to diphenyldisulfide.<sup>12</sup>

In the present study, we report the preparation of Cu NPs supported on D NPs (Cu/DH) and their catalytic activity in the reduction of olefins using hydrazine hydrate as a reducing agent. The advantages of this method are low catalyst loading, short reaction time, cost effectiveness of the catalyst and high product selectivity.

The characterization data of Cu/DH prepared under identical conditions as reported here by powder XRD, diffuse reflectance spectroscopy, X-ray photoelectron spectroscopy, FT-IR and high resolution transmission microscopy have been already reported.<sup>12</sup> The textural properties of various supports are given in Table S1 (ESI<sup>‡</sup>). Further, activated carbon (AC), graphite (G) and multiwalled carbon nanotubes (MWCNT) were also subjected to the same treatment as D NPs followed by deposition of Cu NPs (Table S2, Fig. S2-S12, ESI<sup>‡</sup>). It has been found that pretreatment of commercial D NPs with Fenton reagents is necessary in order to remove amorphous carbon soot from commercial D NPs.11 The average particle size of Cu in DH, ACH, GH and MWCNTH was 3.7, 7.9, 7.8 and 7.3 nm, respectively, according to TEM. The structural integrity of D, G and MWCNT was maintained during the above treatments as evidenced from powder XRD (Fig. S17-S19, ESI<sup>‡</sup>). The interest in D NPs as a support is because of the inertness of their surface compared to other carbon forms or metal oxides. This inertness is particularly interesting when highly reactive intermediates (such as •OH radicals generated from H<sub>2</sub>O<sub>2</sub> already reported in the literature<sup>11</sup>) or reagents (such as hydrazine studied here) that tend to decompose spuriously without forming the desirable active species are involved.

In preliminary experiments, styrene was selected as a model substrate to optimize the reaction conditions. In the absence of a catalyst 7% conversion of styrene was observed using hydrazine hydrate as a reducing agent. Using Cu/D as a catalyst, the styrene conversion reached to 64% with 99% selectivity in 3 h (entry 2, Table 1). Under the same reaction conditions, Cu/DH resulted in 100% conversion and selectivity in 3 h (entry 3, Table 1). Fig. 1 shows the temporal profile for this reaction. On the other hand,

Instituto Univ. de Tecnología Química CSIC - UPV and Departamento de Química, Univ. Politécnica de Valencia, Av. De los Naranjos s/n, 46022 Valencia, Spain. E-mail: hearcia@aim.uvv.es. admeuru@email.com: Fax: +34 9638 7807

 $<sup>\</sup>dagger$  Dedicated to Prof. Miguel A. Miranda with admiration and gratitude on the occasion of his 60th anniversary.

<sup>&</sup>lt;sup>‡</sup> Electronic supplementary information (ESI) available: Preparation of catalysts, experimental procedures, and productivity data. See DOI: 10.1039/c3cc39011j

Table 1Hydrogenation of styrene to ethylbenzene using hydrazine as areducing agent promoted by various catalysts<sup>a</sup>

Run	Catalyst	Time (h)	Conversion <sup><math>b</math></sup> (%)	Selectivity <sup>b</sup> (%)
1	_	3	7	>99
2	Cu/D	3	64	>99
3	Cu/DH	3	100	>99
4	Cu/DH 2nd use	3	97	>99
5	Cu/DH 3rd use	3	95	>99
6	Cu/DH 4th use	3	94	>99
7	$Cu/DH^{c}$	1	5	100
8	$Cu/DH^{c}$	16	35	100
9	$Cu/DH^{c}$	50	100	100
10	$Cu/DH^d$	130	100	100
11	Cu/ACH	3	35	99
12	Cu/GH	3	32	99
13	Cu/MWCNTH	3	47	99
14	Au/DH	3	18	99
15	Au/DH	23	78	99
16	Au/DH	36	100	99
17	Pd/DH	36	94	99

<sup>*a*</sup> Reaction conditions: styrene (1 mmol), catalyst (20 mg),  $N_2H_4\cdot H_2O$  (0.1 mL), aq. NH<sub>3</sub> (0.025 mL), ethanol (4 mL), 60 °C. <sup>*b*</sup> Determined by GC. <sup>*c*</sup> Styrene (20 mmol), Cu/DH (20 mg),  $N_2H_4\cdot H_2O$  (2 mL), aq. NH<sub>3</sub> (0.5 mL), ethanol (20 mL), 60 °C. <sup>*d*</sup> Styrene (50 mmol), Cu/DH (20 mg),  $N_2H_4\cdot H_2O$  (4 mL), aq. NH<sub>3</sub> (0.75 mL), ethanol (40 mL), 60 °C.



Fig. 1 Temporal profile for the reduction of styrene to ethylbenzene using no catalyst (a), and using Cu/GH (b), Cu/ACH (c), Cu/MWCNTH (d) and Cu/DH (e) as catalysts.

Cu/ACH, Cu/GH and Cu/MWCNTH showed lower activity (Table 1, entries 11–13) than Cu/DH suggesting the beneficial effect of DH as a support for Cu NPs. These results indicate that large Cu NPs present in other supports different from DH (see Table S2, ESI‡) are detrimental for the catalytic activity and that Fenton treatment did not improve the catalytic activity for these catalysts in contrast to the case of D (Table S3, ESI‡). In fact, Cu NPs deposited on AC, G, MWCNT without any treatment exhibited even slightly higher activity than with Fenton purification and hydrogen annealing treatment.

We were also interested in comparing the catalytic activity of Cu/DH with Au/DH and Pd/DH at the same metal loading for the reduction of styrene to ethylbenzene (Fig. 2). Interestingly, Cu/DH outperforms Au/DH in terms of initial reaction rate and final conversion. The former catalyst gave complete conversion of styrene in 3 h while the latter catalyst required 36 h to complete the reaction. Hence, the higher activity of the Cu/DH catalyst over Au/DH in the hydrogenation of styrene could be attributed to the ability of the Cu/DH catalyst to favour the formation of diimide<sup>13-15</sup> which is supposed to be the intermediate during the reaction. Further, Pd/DH (Fig. S13, ESI‡)



**Fig. 2** Time conversion plot for the reduction of styrene to ethylbenzene using Cu/DH (a), Au/DH (b), and Pd/DH as catalysts. In all cases, the selectivity of ethylbenzene was more than 99%.

showed comparable activity to that of Au/DH and the two samples were significantly less active than Cu/DH (Fig. 2).

The heterogeneity of the reaction was studied by performing reduction of styrene to ethylbenzene using Cu/DH as a catalyst under the present reaction conditions. After 36% conversion, the catalyst was removed from the reaction mixture by hot filtration, allowing the reaction to continue in the absence of the catalyst. After 3 h, styrene conversion was increased to 42% suggesting that Cu NPs are not leached from the support during the course of reaction and ICP-AES showed the presence of 1 ppm of Cu in the filtrate. Also, the chemical analysis of Cu/DH revealed that the Cu content was maintained. It can be seen that the catalyst could be used for three additional runs without much activity decrease. The kinetic data (Fig. S14, ESI‡) revealed that the catalyst exhibits similar activity having the same turnover frequency for the four runs with the value being  $368 h^{-1}$  suggesting catalyst stability. The average Cu NPs size in Cu/DH after the third use was found to be 3.8 nm (Fig. S2, ESI‡), which is almost similar to that of the fresh catalyst.

It has been reported earlier that the formation of diimide (the presumed hydrogenating species) required either  $H_2O_2$  or air in the presence of a transition metal catalyst.<sup>16,17</sup> Under the present experimental conditions with Cu/DH as a catalyst in air, it can be assumed based on the literature that hydrazine undergoes oxidation to diimide<sup>16,17</sup> which transfers hydrogen to styrene resulting in the formation of ethylbenzene. To ascertain this hypothesis, a control experiment using Cu/DH as a catalyst under a nitrogen atmosphere showed 2% styrene conversion in 3 h. At this point, nitrogen was removed and the reaction continued in the presence of air showing 90% styrene conversion in 3 h (Fig. S15, ESI†). This indirectly supports that diimide is acting as a reagent in the reduction of styrene (Scheme 1).

The productivity and catalyst stability under our experimental conditions were tested by performing the reduction in a large excess of styrene (50 mmol). The reaction was monitored at different time intervals and the time conversion plot is shown



**Scheme 1** Proposed mechanism for the reduction of styrene to ethylbenzene using Cu/DH as a catalyst.



Fig. 3 Productivity test for the reduction of styrene to ethylbenzene at the 50 mmol scale. The reaction conditions are given in Table 1. For the 20 mmol scale, see Fig. S16 (ESI<sup>‡</sup>).

Table 2 Reduction of various olefins catalyzed by Cu/DH<sup>a</sup>

Run	Substrate	Time (h)	Conversion <sup><math>b</math></sup> (%)	Selectivity <sup>b</sup> (%)
1	Styrene	3	100	>99
2	4-Fluorostyrene	8	100	99
3	4-Chlorostyrene	8	99	99
4	4-Methoxystyrene	30	60	99
5	3-Nitrostyrene	8	99	98 <sup>c</sup>
6	Ethyl 4-nitrocinnamate	10	89	99
7	α-Methylstyrene	10	99	98
8	4-Vinylstyrene	6	94	98
9	4-Vinylpyridine	8	95	99
10	Cyclooctene	8	99	99
11	9-Vinylanthracene	24	88	98
12	9-Vinylcarbazole	14	99	99
13	<i>N</i> -Vinylcaprolactam	33	96	99
14	Vinylcyclooctane	5	99	99
15	2-Vinylnapthalene	4	99	99
16	2-Cyclohexen-1-ol	23	95	99
17	Phenylacetylene	24	39	$61^d$
18	Allylphenyl sulfide	8	99	96 <sup>e</sup>
19	Phenyl vinyl sulfide	9	99	98
20	Allylphenyl ether	5	99	99

<sup>*a*</sup> Reaction conditions: substrate (1 mmol), catalyst (20 mg), N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (0.1 mL), aq. NH<sub>3</sub> (0.025 mL), ethanol (4 mL), 60 °C. <sup>*b*</sup> Determined by GC. <sup>*c*</sup> 2% of 3-aminoethylbenzene was also formed. <sup>*d*</sup> Selectivity corresponds to styrene and 39% of ethylbenzene was observed. <sup>*e*</sup> 3% of diphenyldisulfide was observed.

in Fig. 3. It is interesting to note that the reduction of styrene to ethylbenzene was completed in 130 h. The turnover number for this reaction under these conditions was 30 617 cycles.

These results with styrene prompted us to check the scope of Cu/DH as a catalyst with other substrates. 4-Fluoro, 4-chloro and 3-nitrostyrenes with electron withdrawing substrates were reduced to their corresponding substituted ethylbenzenes with high conversion and selectivity in 8 h while 4-methoxystyrene with a strong electron donating substituent required 30 h to reach 60% conversion with very high selectivity.

The present catalytic system showed very high chemoselective reduction in the case of 3-nitrostyrene. A similar behavior was observed with ethyl 4-nitrocinnamate resulting in 89% conversion in 10 h with high selectivity towards the reduction of C=C double bonds. On the other hand,  $\alpha$ -methylstyrene resulted in 99% conversion with 98% selectivity in 10 h. Further, 4-vinylstyrene was reduced to 1,4-diethylbenzene with 98% selectivity in 6 h. A cyclic olefin namely cyclooctene was also reduced to cyclooctane with 99% conversion and selectivity in 8 h. Vinyl substituted heterocyclic compounds were reduced to their corresponding products with very high conversion and selectivity (entries 9, 12 and 13, Table 2). For example, vinylcyclooctane was reduced to ethylcyclooctane with 99% conversion and selectivity in 5 h. 2-Cyclohexen-1-ol was reduced to cyclohexanol, an important intermediate for the synthesis of nylon-66, with 95% conversion and 99% selectivity in 23 h. An attempt to reduce phenylacetylene showed a mixture of 61% styrene and 39% ethylbenzene at 39% conversion in 24 h. On the other hand, allylphenyl sulfide was reduced to phenylpropyl sulfide with 99% conversion and 96% selectivity in 8 h. Similarly, phenyl vinyl sulfide showed high conversion (99%) and selectivity towards ethyl phenyl sulfide in 9 h. Allyl phenyl ether was also reduced to phenyl propyl ether in 5 h with 99% conversion and selectivity.

In conclusion, Cu/DH exhibited higher catalytic activity than its analogous catalyst Au/DH and Pd/DH for the reduction of styrene to ethylbenzene. Further, Cu NPs supported on ACH, GH and MWCNTH showed lower activity than Cu/DH suggesting the beneficial role of DH as a support. Hydrogen annealing improves the performance of D as support probably by decreasing the population of carboxylic groups, thus leading to smaller Cu NPs. The catalyst could also be reused without much loss in its activity and exhibited higher productivity by giving a high turnover number, Cu being a cheaper transition metal than Pd and Au.

Financial support from the Spanish Ministry of Science and Education (Consolider MULTICAT, CTQ-2012-32316) is gratefully acknowledged.

## Notes and references

- 1 J. G. de Vries and C. J. Elsevier, Handbook of homogeneous hydrogenations, Wiley-VCH, New York, 2007.
- 2 W. M. N. Ratnayake, J. S. Grossert and R. Ackman, J. Am. Oil Chem. Soc., 1990, 67, 940.
- 3 D. J. Pasto and R. T. Taylor, *Reductions with Diimide*, in *Organic Reactions*, ed. V. L. A. Paquette, Wiley & Sons, New York, 1991, vol. 40, p. 91.
- 4 E. W. Schmidt, Hydrazine and Its Derivatives: Preparation, Properties, and Applications, Wiley & Sons, New York, 2nd edn, 2001, vol. 1, p. 475.
- 5 M. Lamani, R. Siddappa, S. Guralamata and K. R. Prabhu, *Chem. Commun.*, 2012, 48, 6583.
- 6 Y. Imada, H. Iida and T. Naota, J. Am. Chem. Soc., 2005, 127, 14544.
- 7 A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *Adv. Synth. Catal.*, 2009, **351**, 2271.
- 8 M. Shokouhimehr, Y. Piao, J. Kim, Y. Jang and T. Hyeon, *Angew. Chem.*, *Int. Ed.*, 2007, **46**, 7039.
- 9 E. Kim, S. Kim and B. M. Kim, Bull. Korean Chem. Soc., 2011, 32, 3183.
- 10 A. Dhakshinamoorthy and K. Pitchumani, *Tetrahedron Lett.*, 2008, 49, 1818.
- 11 S. Navalon, R. Martin, M. Alvaro and H. Garcia, *Angew. Chem., Int. Ed.*, 2010, **49**, 8403.
- 12 A. Dhakshinamoorthy, S. Navalon, D. Sempere, M. Alvaro and H. Garcia, *ChemCatChem*, 2013, 5, 241–246.
- 13 E. J. Corey, W. L. Mock and D. J. Pasto, *Tetrahedron Lett.*, 1961, 2, 347.
- 14 E. J. Corey, D. J. Pasto and W. L. Mock, J. Am. Chem. Soc., 1961, 83, 2957.
- 15 S. Hunig, H. R. Muller and W. Thier, Angew. Chem., Int. Ed. Engl., 1965, 4, 271.
- 16 S. Hunig, H. R. Muller and W. Thier, Angew. Chem., Int. Ed. Engl., 1965, 4, 271.
- 17 Y. Imada, H. Iida, T. Kitagawa and T. Naota, *Chem.-Eur. J.*, 2011, 17, 5908.