Journal of
Nanoscience and Nanotechnology
Vol. 13, 4990–4995, 2013

Application of Gallium Nitride Nanostructures and Nitrogen Doped Carbon Spheres as Supports for the Hydrogenation of Cinnamaldehyde

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This paper reports on the synthesis and use of nanostructures of gallium nitride (GaN NSs) and nitrogen doped carbon spheres (NCSs) as support materials for the hydrogenation of cinnamaldehyde. This study provides the first investigation of GaN as a catalyst support in hydrogenation reactions. The GaN NSs were synthesized via chemical vapour deposition (CVD) in a double stage furnace (750 °C) while NCSs were made by CVD in a single stage furnace (950 °C) respectively. TEM analysis revealed that the GaN NSs were rod-like with average diameters of 200 nm, while the NCSs were solid with smoother surfaces, and with diameters of 450 nm. Pd nanoparticles (1 and 3% loadings) were uniformly dispersed on acid functionalized GaN NSs and NCS. The Pd nanoparticles had average diameters that were influenced by the type of support material used. The GaN NSs and NCSs were tested for the selective hydrogenation of cinnamaldehyde in isopropanol at 40 and 60 °C under atmospheric pressure. A comparative study of the activity of the nanostructured materials revealed that the order of catalyst activity was 3% Pd/GaN $>$ 3% Pd/NCSs $>$ 1% Pd/NCSs $>$ 1% Pd/GaN. However, 100% selectivity to hydrocinnamaldehyde (HCALD) was obtained with 1% Pd/GaN at reasonable conversion rates.

Keywords: Gallium Nitride Nanostructures, N-Doped Carbon Spheres, Palladium, Hydrogenation, Cinnamaldehyde, Catalyst Supports.

1. INTRODUCTION

The selective hydrogenation of α,β-unsaturated aldehydes is of interest due to the wide industrial applications of their corresponding hydrogenation products in the fine chemicals and pharmaceuticals industries.[1] The hydrogenation of α,β-unsaturated aldehydes to generate α,β-unsaturated alcohols and saturated alcohols depends on the method used to prepare the catalysts, the amount of catalyst used, the type of support, the catalyst precursors, solvents, additives (or promoters) and the reaction conditions employed e.g., temperature.[2] A standard reaction used to evaluate catalysts and supports is the hydrogenation of cinnamaldehyde (CALD) (Fig. 1). CALD hydrogenation can yield hydrocinnamaldehyde (HCALD), cinnamyl alcohol (CALC) and 3-phenyl-1-propan-1-ol (3P1P) and thus provides a range of easily identifiable (and important) chemicals to evaluate catalyst behaviour.[3]

HCALD is of interest because it has been found to be an important intermediate for the preparation of chemicals used in the treatment of the HIV. It is also commonly used as an additive in the food industry as a flavouring agent.[3] CALC is also an important chemical but the production of CALC via selective hydrogenation is a difficult task because the formation of the saturated aldehyde is thermodynamically favoured over that of the unsaturated alcohol.[4] Considerable efforts have been made to search for a catalytic system that is able to actively and selectively carry out the preferential hydrogenation of the C=O bond in the presence of a conjugate C=C bond.[5] Selectivity towards the unsaturated alcohol can be improved significantly using designed heterogeneous catalysts.[4] Previous studies have shown that it is much easier to hydrogenate the unsubstituted isolated C=C bond than to hydrogenate

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1533-4880/2013/13/4990/006 doi:10.1166/jnn.2013.7578

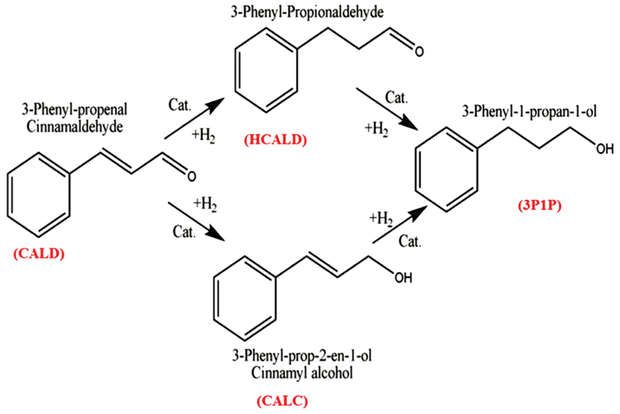

Fig. 1. Reaction scheme proposed for the selective hydrogenation of cinnamaldehyde.[12]

the isolated C=O aldehydic or ketonic group.[6] The hydrogenation of CALD in polar solvents is known to favour the transformation of the C=O bond, while hydrogenation in non-polar solvents favours transformation of the C=C bond.[7] Further hydrogenation of CALC and HCALD produces 3P1P (Fig. 1). While also a useful chemical, the products HCALD and CALC are the target compounds in this reaction.

Many catalysts (e.g., Pd on carbon nanotubes) have been reported for the hydrogenation of CALD but selectivity to the final required products remains a challenge.[3, 8–11] Indeed, carbon supported Pd catalysts are known to be one of the most effective catalysts for the selective hydrogenation of the C=C bond.[3] Thus, carbon supported Pd catalysts provide a measure of the catalyst selectivity of other Pd supported catalysts.

We have recently commenced a study to investigate the use of classical semiconductors as supports in heterogeneous catalysis. It is believed that the semi-conducting power of a support will affect the metal-support interaction and hence influence the activity and selectivity of a metal catalyst. The new synthetic strategies that allow for the synthesis of nano shaped/sized semi-conductors thus opens up the use of these materials as catalyst supports. These studies will thus complement the typical studies of semiconductors as sensors etc.

In the first of these studies we have explored the synthesis and use of nano GaN as catalyst support for hydrogenation reactions. GaN is a stable material at high temperatures and it is not easily oxidized to gallium oxide or reduced to Ga metal by oxidizing or reducing atmospheres. The ability to make nanoscale GaN, as seen with other nanomaterials, gives high surface area GaN with tunable electrical and optical properties, making it a good candidate for various applications including catalysis; hence our choice to exploit its ability to act as a support material for Pd catalysts.

As mentioned earlier, Pd/C catalysts provide a good model for comparing with other catalyst/support combinations. In earlier studies we have shown that nitrogen (N) doping of carbons leads to better catalyst stability/activity than when undoped carbons are used. We have thus chosen to use N doped carbon spheres (NCSs) as our model system. These are easy to prepare and are easy to study by electron microscopy techniques. In this work, we have thus compared Pd/GaN NSs and Pd/NCSs (1 wt% and 3 wt% Pd loadings) for the preferential selective hydrogenation of CALD to the corresponding saturated aldehyde (HCALD) at different temperatures under atmospheric pressure.

2. EXPERIMENTAL DETAILS

2.1. Synthesis and Functionalization of GaN Nanostructures

GaN nanorods were synthesized in a quartz tube placed in a two-stage furnace. The first zone (zone 1) of the double stage furnace was heated to 1100 °C to preheat the NH_3 and cause its dissociation into NH_2, NH, and N reactive species. The second reactor zone (zone 2), was heated to 750 °C. Ga_2O_3 powder was placed in a quartz crucible placed in the center of the quartz tube in zone 2. $N_2$was allowed to flow through the quartz tube (to remove air) at a flow rate of 12 ml/min while the two zones of the reactor reached their respective reaction temperatures. When the desired temperatures were reached NH_3, at different flow rates, was introduced. The NH_3 and decomposed NH_3 species reacted with Ga_2O_3 in zone 2 to convert the reactant to GaN NSs. The NH_3 flow rate was varied from 12–210 ml/min while N_2 was kept at the same flow rate. The optimized flow rate used in this study was 210 ml/min. After 2 h, the furnace was cooled to room temperature while N_2 was passed through the reactor. The crucible was then removed from the reactor and weighed to establish the amount of GaN product formed. A piranha solution (i.e., mixture of 0.52 M HNO_3 + 0.12 M H_2SO_4) was used to create functional groups on the GaN NS support prior to catalyst synthesis stage.[13]

2.2. Synthesis and Functionalization of NCSs

The synthesis method for producing NCSs was adopted from Deshmukh et al. with minor modifications.[14] NCSs were synthesized using a non-catalytic CVD method from acetylene (C_2H_2) as a carbon source and acetonitrile (CH_3CN) as the N (and C) source. N_2 was first flowed through the quartz tube (to remove air) at 100 ml/min while the furnace was heated from room temperature to 950 °C at a heating rate of 10 °C/min. Once the desired temperature was attained the N_2 flow was switched off and C_2H_2 was bubbled through the CH_3CN solution (80 °C) at a flow rate of 100 ml/min for 90 minutes. After the required carbonization time, the C_2H_2 was switched off and N_2 was flowed through the system at 100 ml/min until the furnace had cooled down to room temperature. NCSs were then collected from the walls of the quartz tube and weighed. Functionalization of the NCSs was carried out by treatment with 55% nitric acid (HNO_3) for 24 h at 40 °C. The functionalized NCSs were then filtered and washed with deionized water until the pH of the filtrate was neutral. The NCSs were then dried in an oven for 12 h at 80 °C.

2.3. Preparation of Pd/GaN and Pd/NCS Catalysts

The catalysts were prepared using the liquid phase reduction method in an ethylene glycol solution. The supports (500 mg) were placed into a 500 ml round bottomed flask and ethylene glycol (150 ml) was added to the flask. The flask contents were sonicated for 15 min followed by magnetic stirring for 30 min. The metal precursor solution (0.05 M palladium acetate) was then added drop-wise to the mixture of carbon support and ethylene glycol. The concentrations of the precursor solutions in the ethylene glycol solutions were calculated in order to prepare catalysts with metal loadings of 1 and 3 wt%. The resultant solution was magnetically stirred vigorously for a further 3 h at room temperature and then refluxed at 195 °C in an oil bath for 3 h. The solution was then cooled to room temperature. The resultant solution was filtered and thoroughly washed with 20 ml of acetone followed by excess distilled water. The supported metal catalysts were dried in air for 8 h at 80 °C and then ground in a mortar to form a powder.

2.4. Characterization of the Supports and Catalysts

The structural morphology of the support materials and catalysts was ascertained by transmission electron microscopy (FEI Tecnai G^2 Spirit electron microscope at 120 kV). Powder X-ray diffraction (Bruker D2 Phaser) was used to study the chemical composition and crystallinity of the materials. A Brunauer–Emmett–Teller (BET) TRISTAR 3000 analyzer was used to measure the surface area and porosity of the catalysts.

2.5. Hydrogenation of Cinnamaldehyde

Hydrogenation of CALD was carried out in a three necked round bottomed flask. The catalyst (0.01 g) and a 0.01 M CALD (dissolved in solvent) were added into the reaction flask. The air inside the system was expelled by passing N_2 through the flask for 30 min while the contents were heated to the required temperature. After this, hydrogen gas (50 ml/min) was bubbled through the system while the flask contents were stirred. The course of the reaction was monitored by withdrawing liquid samples from the flask every hour for 6 h. The products were analyzed on a gas chromatogram equipped with an FID detector. The column used was a ZB-1 capillary column (30 m × 0.53 mm × 1.5 μm). Reaction products were identified by comparison with authentic GC standards of CALD, HCALD, 3P1P, and CALC.

3. RESULTS AND DISCUSSION

3.1. XRD and TEM Analysis

Powder XRD was used to study the chemical composition and purity of the GaN NSs and NCSs. Figure 2 shows that the as-synthesized materials were the required materials. The peaks observed in Figure 2(a) were indexed and found to correspond to crystalline hexagonal lattice planes of the wurzite structure of GaN. In Figure 2(b), the two diffraction peaks at 25.5° and 43.3° correspond to the (002) and (101) hexagonal lattice planes of graphitic carbon respectively.[15]

Since the materials were relatively free of impurities no purification process was required. However, it was necessary to modify the surface of the materials through acid treatments to make them dispersible in solution and to allow uniform dispersion of Pd catalysts on the supports. This step impacted on the Pd-support interaction and hence the dispersion and activity of the Pd. We have shown in our previous studies on carbon nanotubes that the degree of functionalization of the support materials affects the activity of the catalyst.[15]

The TEM images of the GaN and NCS supports revealed the rod like structure of the GaN (comprised of smaller particles) and the spherical shape of NCSs (not shown here).

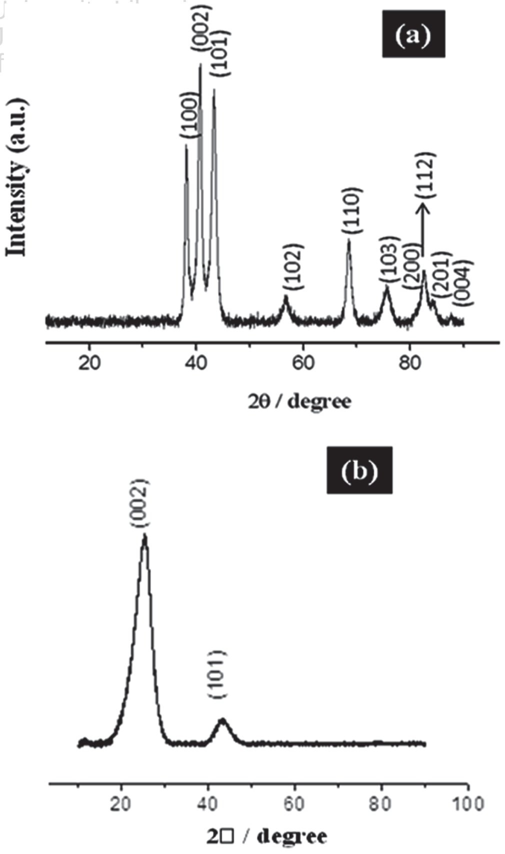

Fig. 2. PXRD patterns of (a) as-synthesized GaN NSs (synthesis temp = 750 °C) and (b) as-synthesized NCSs.

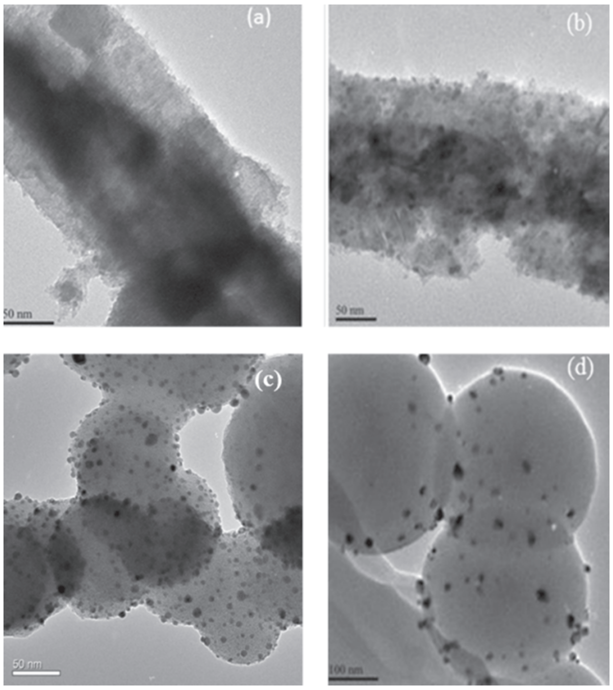

Fig. 3. TEM images of (a) 1% Pd/GaN, (b) 3%Pd/GaN, (c) 1%Pd/NCSs and (d) 3%Pd/NCSs. The dark spots are Pd nanoparticles.

The TEM images of the four Pd supported samples studied (1% Pd/GaN; 3% Pd/GaN; 1% Pd/NCSs and 3% Pd/NCSs) are shown in Figure 3. The Pd loaded on the NCSs can readily be seen while the Pd loaded on the GaN is more difficult to observe due to

(i) the small Pd particle size
(ii) the distribution of Pd on the rough surface and
(iii) the colour contrast of Pd and GaN.

The Pd nanoparticles were found to be well dispersed on the surface of the nanostructures with an average size range of between 4–15 nm. The Pd particle sizes were smaller on the GaN than on the NCSs (Fig. 4). For example 3% Pd/GaN gave Pd particles with an average diameter of 10 nm, while the diameters of the Pd on the 3% Pd/NCSs were 15 nm (Fig. 4). The 1% Pd/NCS catalysts had Pd average particle sizes of 4.7 nm; the Pd on the 1% Pd/GaN was difficult to see and thus a meaningful particle size analysis could not be achieved. As the loading of Pd was increased, agglomeration occurred and larger particles formed, and the average particle size increased.[16]

3.2. BET Surface Area Analysis

Table I shows the surface areas and pore volumes of the supports and catalysts. Comparison of the surface areas of the supports revealed that the GaN NS had a higher surface area (~20 m^2/g) than the NCSs (~1 m^2/g). The surface area increased when the Pd was added to the support materials. The highest surface area (i.e., 63.5 m^2/g) was observed with the 3% Pd/GaN catalyst. This suggests that most of Pd nanoparticles that were deposited on the surface did not block any of the mesopores.[17] The higher surface area of GaN would suggest a better dispersion of Pd particles on GaN than NCSs (as seen for the 3% loaded sample).

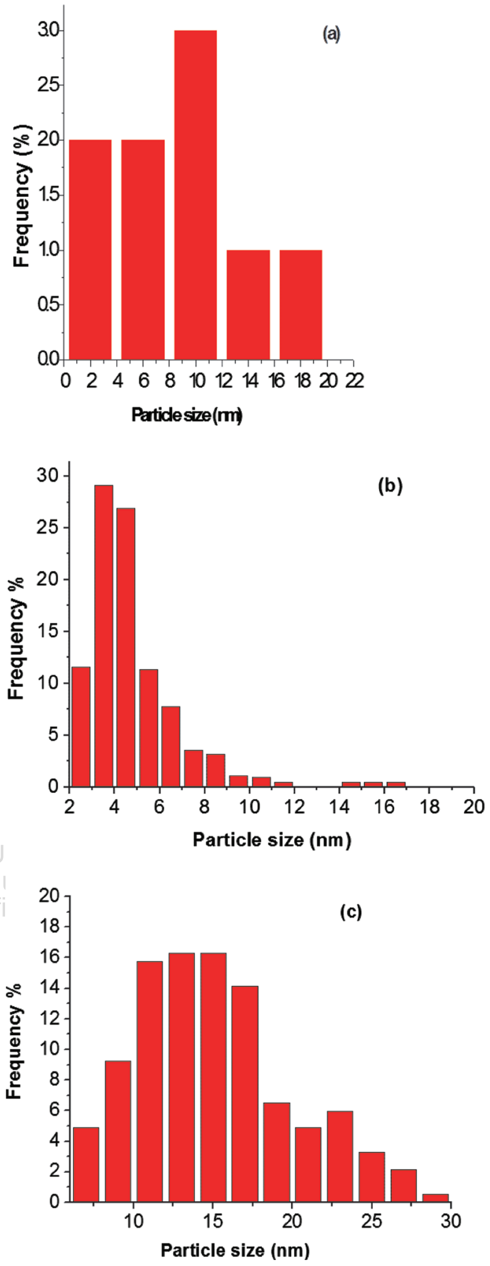

Fig. 4. Particle size distribution graphs of (a) 3% Pd/GaN, (b) 1% Pd/NCSs and (c) 3% Pd/NCSs.

3.3. Comparison of Catalyst Activity: Cinnamaldehyde Hydrogenation

Figure 5 and Table II shows the CALD hydrogenation results using a 1% wt loading of Pd on the GaN and NCS supports carried out at reaction temperatures of 40 and

Table I. BET surface areas and pore volumes of the supports and catalysts.

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)
GaN	19.6	0.01
NCSs	1.5	0.003
1% Pd/GaN	23.9	0.1
1% Pd/NCSs	3.8	0.07
3% Pd/GaN	63.5	0.02
3% Pd/NCSs	4.2	0.02

Table II. A summary of the % CALD conversions and selectivities of the Pd/GaN and Pd/NCSs catalysts using different Pd loadings and reaction temperatures.

Catalyst	Temperature (°C)	CALD conversion (%)	Product selectivity (%)[a]	
			HCALD	3P1P
1% Pd/GaN	40	8	100	0.00
	60	23	100	0.00
1% Pd/NCSs	40	27	86	14
	60	61	94	5.6
3% Pd/GaN	60	97	86	13.9
3% Pd/NCSs	60	60	90	9.5

Note: [a]No CALC observed.

60 °C. The 1% Pd/GaN catalyst gave lower conversions at both temperatures when compared to the 1% Pd/NCSs catalyst. This was unexpected as the Pd particles are smaller on the GaN and hence the dispersion and turnover number would be expected to be larger on the GaN. This suggests a strong Pd-GaN interaction (relative to the Pd-NCS interaction) that modifies the catalyst behaviour. This was also suggested by the selectivity data—the Pd/GaN does not over hydrogenate the HCALD to 3PIP.

In an attempt to increase the catalyst activity 3% Pd loaded catalysts were studied (Fig. 6, Table II). The 3% loaded catalysts show superior activity as expected but a reduced selectivity to the HCALD. At 60 °C the 3% Pd/GaN has a slightly higher activity than the 3% Pd/NCS catalyst, but the reason for this is not obvious. Figure 6(b) indicates that this is true throughout the full reaction timeframe. The selectivity data suggest that there is little difference between the two catalysts. It appears that the HCALD/3PIP ratio did not vary with time on stream (or conversion), perhaps suggesting that the secondary hydrogenation step only occurs when the CALD is bound to the Pd.

The data thus suggest that the Pd was bound to the CALD and provided the interaction is strong enough conversion to HCALD occurs. Not unexpectedly, any $\mathrm{C{=}O}$–Pd interactions must be weak as no CALC was formed in the reaction. Once the $\mathrm{C{=}C}$ bond has been hydrogenated the HCALD-Pd intereaction must be weak and the product will dissociate from the Pd. At the higher temperatures 3PIP is formed. Thus the size of the Pd particle and the Pd-support interaction detemine the course of the reaction. In future studies the stability of the catalyst will be evaluated under the reaction conditions.

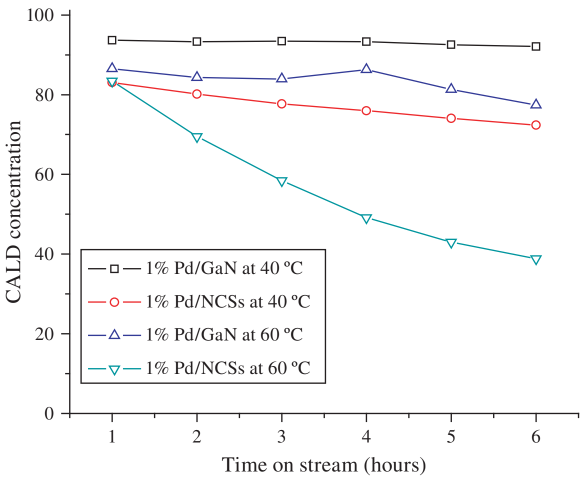

Fig. 5. Graphs showing CALD remaining as a function of time on stream at 40 and 60 °C for 1% Pd/GaN and 1% Pd/NCSs catalysts.

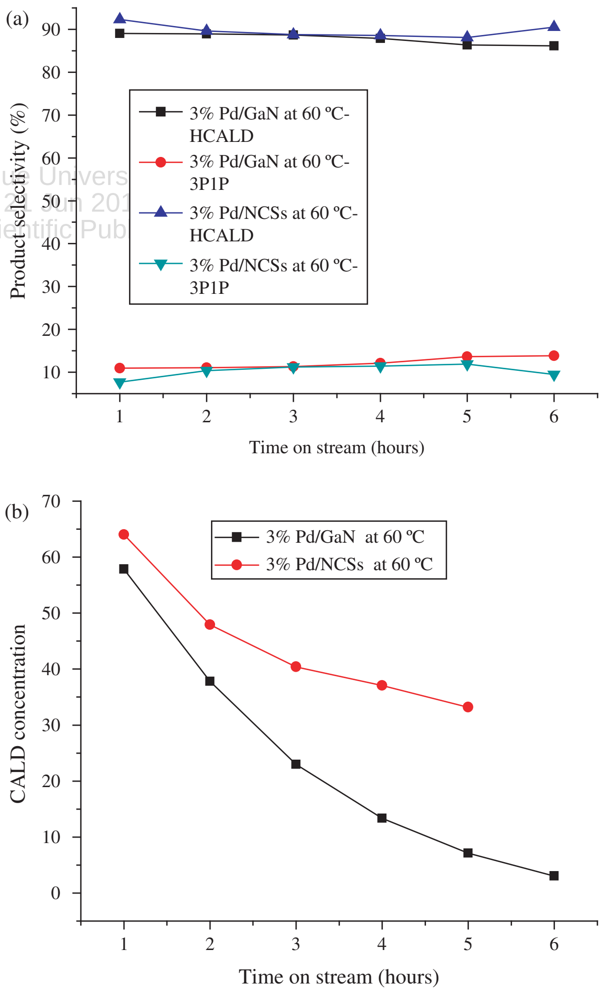

Fig. 6. Graphs showing (a) the product selectivity to HCALD and 3P1P (b) CALD remaining as a function of time on stream at 60 °C for 3%Pd/GaN and 3% Pd/NCSs catalysts.

4. CONCLUSIONS

This study has shown for the first time that GaN NSs can be used as support materials for Pd nanoparticles for the hydrogenation of CALD. The data revealed that the GaN inhibits the hydrogenation relative to NCSs and in doing so gives a catalyst with better selectivity to HCALD. Higher conversions of CALD and poorer selectivity towards HCALD were obtained using the 3% Pd/GaN and 3% Pd/NCSs catalysts. TEM images showed that the Pd metal nanoparticles are well dispersed on the surface of the support materials and that small Pd particles give lower conversions but higher selectivities. The uniform dispersion of the Pd nanoparticles was achieved by support functionalization using different acid treatments. The GaN NSs can thus be used as supports for catalytic reactions in solution (and presumably in the gas phase). This study suggests that the use of GaN NSs may not only be used in electronic applications but can also be exploited in heterogeneously catalysed reactions such as this one. The interaction between the Pd nanoparticles and the GaN NSs is yet to be established.

Acknowledgments: The authors would like to thank the University of the Witwatersrand, the Council for Scientific and Industrial Research (Pretoria), Carnegie Corporation (University of the Witwatersrand), the DST/NRF Centre of Excellence in Strong Materials (CoE-SM) and DST/NRF Nano—Architecture Flagship Program in the beneficiation of platinum group metals for financial support. The work was also conducted with support from the DST/NRF South Africa–India bilateral (grant number 76157).

References and Notes

1. L. Zhang, M. Winterbotton, A. P. Boyes, and S. Raymahasay, *J. Chem. Tech. Biotechnol.* 72, 264 (**1998**).
2. U. K. Singh and M. A. Vannice, *Appl. Catal. A: General* 213, 1 (**2001**).
3. C. Ge, Y. Li, J. Zhao, and R. Zhou, *Ind. J. Chem.* 49A, 281 (**2010**).
4. A. B. Merlo, B. F. Machado, V. Vetere, J. L. Faria, and M. L. Casella, *Appl. Catal. A: General* 383, 43 (**2010**).
5. M. Lashdaf, A. O. I. Krause, M. Lindblad, M. Tiitta, and T. Venalainen, *Appl. Catal. A: General* 241, 65 (**2003**).
6. H. Chen, X. Li, M. Wang, and Y. Xu, *Appl. Catal. A* 225, 117 (**2002**).
7. H. Yamada and S. Goto, *J. Chem. Eng. Japan* 36, 586 (**2003**).
8. H. Vu, F. Goncalves, R. Philippe, E. Lamouroux, M. Corrias, Y. Kihn, D. Plee, P. Kalck, and P. Sero, *J. Catal.* 240, 18 (**2006**).
9. Y. Li, G.H. Lai, and R. X. Zhou, *Appl. Surf. Sci.* 253, 4987 (**2007**).
10. H. X. Ma, L. C. Wang, L. Y. Chen, C. Dong, W. C. Yu, T. Huang, and T. Y. Qian, *Catal. Commun.* 8, 452 (**2007**).
11. A. Corna, H. Garcia, and A. Leyva, *J. Mol. Catal. A: Chem.* 230, 97 (**2005**).
12. K.-Y. Jao, K.-W. Liu, Y.-W. Yang, and A.-N. Ko, *J. Chin. Chem. Soc.* 56, 885 (**2009**).
13. C. W. Hsu, C. P. Chen, C. C. Kuo, P. P. Paskov, P. O. Holtz, L. C. Chen, and K. H. Chen, *J. Appl. Phys.* 109, 053523 (**2011**).
14. A. A. Deshmukh, R. Ul. Islam, M. J. Witcomb, W. A. L. van Otterlo, and N. J. Coville, *Chem. Cat. Chem.* 2, 51 (**2010**).
15. M. A. M. Motchelaho, H. Xiong, M. Moyo, L. L. Jewell, and N. J. Coville, *J. Mol. Catal. A: Chemical* 335, 189 (**2011**).
16. Y. Liao, L. Gao, X. Zhang, and J. Chen, *Mater. Res. Bulletin* 47, 1625 (**2012**).
17. M. Moyo, M. A. M. Motchelaho, H. Xiong, L. L. Jewell, and N. J. Coville, *Appl. Catal. A: General* 413–414, 223 (**2012**).

Received: 31 October 2012. Accepted: 12 February 2013.