Catalysis Science & Technology

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/catalysis

Journal Name

COMMUNICATION

Highly dispersed nanodiamonds supported on few-layer graphene as robust metal free catalysts for ethylbenzene dehydrogenation reaction

Received 00th January 20xx,

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Jiangyong Diao,[a] Hongyang Liu,*[a] Zhenbao Feng,[a] Yajie Zhang,[a] Tong Chen,[b] Changxi Miao,[b] Weimin Yang*[b] and Dang Sheng Su*[a]

Highly dispersed nanodiamond (ND) aggregates with sizes ranging from 5 - 50 nm supported on few-layer graphene are successfully prepared for ethylbenzene dehydrogenation to styrene. The as-prepared ND/graphene catalyst presents higher catalytic performance than that of commercial ND powders, showing its potential application as a metal free catalyst in chemical industry.

Nanodiamond (ND) has received considerable attention due to the various possible applications such as luminescence imaging, drug delivery and quantum engineering.[1-6] It has been demonstrated that the ND is a promising heterogeneous catalyst in catalytic dehydrogenation of ethylbenzene (EB) to styrene (ST). The distinct catalytic performance makes ND candidate for replacing the traditional metal oxide catalysts.[7,8] In general, the commercially available ND powders are prepared by a novel explosion method.[9,10] However, the as-prepared ND powders are highly detrimental to be used in fixed-bed reactors for industrial applications.[11] In addition, the commercial ND powders are complex conglomerates consisting of discrete levels of aggregates, which can distinctly decrease the utilizing efficiency of the ND catalyst while used in the dehydrogenation reactions. In order to overcome these disadvantages and improve the utilizing efficiency of the commercial ND powders, several methods have been reported to prepare ND powders into larger objects, such as ND/SiC and ND&CNT/SiC monolithic catalysts, by using macroporous SiC as the monolithic support and commercial ND powders as the active sites.[12-15] Although these achievements have been made in this field, it is still a challenge to develop highly dispersed ND (HD-ND) based catalyst with robust catalytic performance for the EB direct dehydrogenation to ST.

Recently, graphene has been regarded as one of the most interesting materials due to its unique mechanical and electronic properties. In the field of catalysis, graphene-supported catalyst with distinguishing catalytic activity has attracted considerable attentions.[16-20] Herein, in this paper, we report a simple procedure for the fabrication of HD-ND nanoaggregates supported on the few-layer graphene (HD-ND/graphene) for the catalytic dehydrogenation of EB to ST. Firstly, we synthesized HD-ND nanoaggregates with sizes ranging from 5 - 50 nm by milling treatment of commercial ND powders. Then, the obtained HD-NDs were deposited on the few-layer graphene by rotary evaporation using the suspension of HD-NDs dispersed in water. After further drying at 120°C, the as-prepared HD-ND nanoaggregates were evenly and separately distributed on the few-layer graphene support. When the ND weight loading of the HD-ND/graphene catalyst is just 4 wt%, it presents the best catalytic performance than that of commercial ND powders and the pure few-layer graphene support, showing its potential application as a steam free catalyst for the catalytic dehydrogenation reaction of EB to ST.

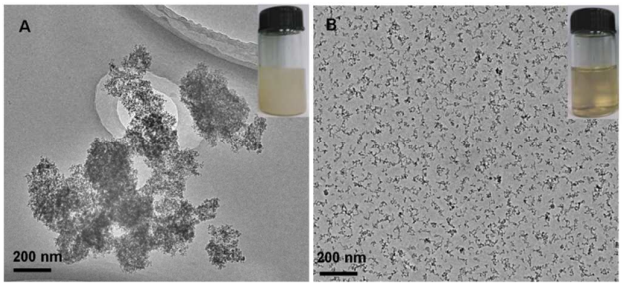


Fig. 1 TEM images of (A) the typical commercial ND powders after sonication for 10 h and (B) highly dispersed ND nanoaggregates. Insets are the corresponding commercial ND powders and highly dispersed ND nanoaggregates suspensions dispersed in water, respectively.

[a] *Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China. E-mail: liuhy@imr.ac.cn, dssu@imr.ac.cn; Fax: +86 2483970019; Tel: +86 2423971577*

[b] *Sinopec Shanghai Research Institute of Petrochemical Technology, 1658 Pudong Beilu, Shanghai, China. E-mail: yangwm.sshy@sinopec.com; Fax: +862168462283; Tel: +862168462824.*

† Electronic Supplementary Information (ESI) available: [Experimental section, TEM results, XRD, Raman and long term test]. See DOI: 10.1039/x0xx00000x

TEM image of the commercially available ND powders dispersed in water after sonicating for 10 h is shown in Fig. 1A. Note that most of the ND aggregates with the sizes under 1 μm can be collected with the assistance of sonication. However, we can still obtain few ND aggregates under 100 nm as presented in Fig. S1A. Generally, the commercially obtained ND powders are complex conglomerates composed by discrete levels of aggregation. Sonication can just help destroy the micro-sized higher aggregates but did not affect the ND aggregates under 1 μm.[21] These micro-sized ND aggregates can distinctly decrease the utilizing efficiency and enhance the cost of the ND catalyst while used in the catalytic reaction. The TEM image of highly dispersed ND nanoaggregates obtained by the further milling process of commercial ND powders is displayed in Fig. 1B. Comparing with the original commercial ND powders (TEM image in Fig. 1A), it can be seen that the HD-ND nanoaggregates sizes ranging from 5 - 50 nm can be successfully prepared by the milling treatment. Meanwhile, it can be still observed that the colour of the obtained HD-ND nanoaggregates in water solution is light brown (inset in Fig. 1B), which is quite different from the gray colour of the initial commercial ND powders (inset in Fig. 1A), further proving that HD-ND nanoaggregates can be facilely obtained by the milling process. The HRTEM image of one single ND nanoparticle displayed in Fig. S1B indicates that the original structure of the HD-ND nanoaggregates is well kept after the milling treatment.

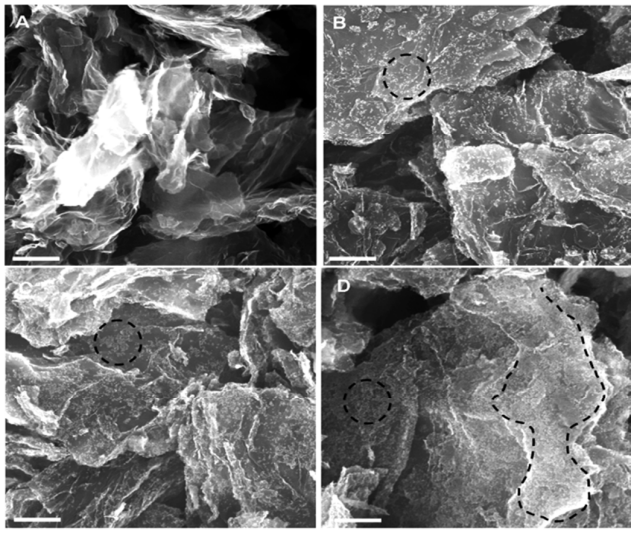


Fig. 2 SEM images of (A) the pure few-layer graphene support, (B) HD-ND/graphene (4 wt%), (C) HD-ND/graphene (12 wt%), HD-ND/graphene (30 wt%). The scale bar is 1 μm.

The HD-ND nanoaggregates supported on few-layer graphene catalysts are prepared by deposition using HD-ND suspensions. The SEM image of the pure few-layer graphene is displayed in Fig. 2A. It can be seen that the graphene sheets are highly folded and self-assembled to a three dimensional morphology. Representative SEM image of HD-ND nanoaggregates supported on the graphene with 4 wt% ND loading is shown in Fig. 2B. Note that the HD-ND nanoaggreagates corresponding to the light nanodots in Fig. 2B are evenly and separately distributed on the graphene surface. And the initial structure of the graphene is well maintained after the deposition of HD-ND nanoaggregates. We also investigate the detailed structure of HD-ND/graphene catalysts with different ND weight loadings. The SEM images of the as-prepared HD-ND/graphene catalysts with 12 wt% and 30 wt% ND loading are displayed in Fig. 2C and Fig. 2D, respectively. As to the catalyst with 12 wt% ND loading, it can be found that parts of the HD-NDs are conglomerated on the graphene surface as marked in Fig. 2C. But for the HD-ND/graphene catalyst with 30 wt% ND loading, a thick ND layer is distinctly covered on the graphene surface (Fig. 2D), revealing that the serious reaggregation of the HD-NDs on the graphene support.

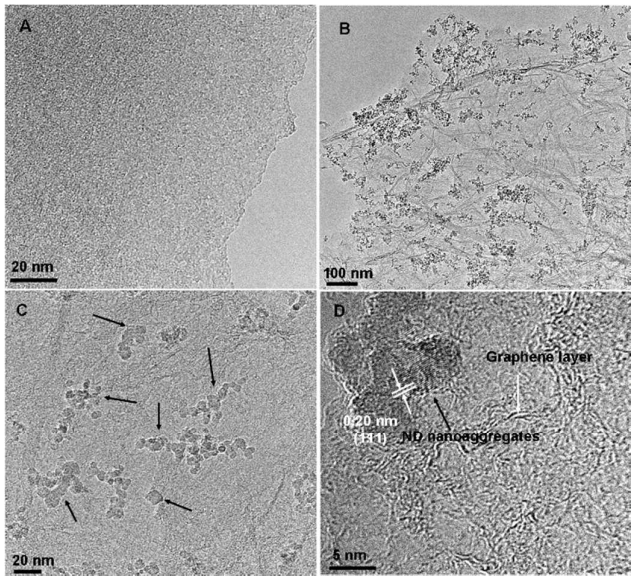


Fig. 3 TEM images of (A) the pure few-layer graphene support, (B) and (C) HD-ND/graphene (4 wt%), (D) high resolution TEM image of the HD-ND nanoaggregates supported on the graphene support.

In order to investigate the detailed structure of the as-prepared HD-ND/graphene catalysts, TEM images of the few-layer graphene and HD-ND/graphene catalysts are displayed in Fig. 3. TEM images of the HD-ND/graphene catalyst with 4 wt% ND loading are presented in Fig. 3B and 3C. Notably, most of the HD-ND nanoaggregates are uniformly supported on the graphene surface, only a few HD-NDs are slightly reaggregated (Fig. 3B), consisting well the SEM observations. Meanwhile, Fig. 3C clearly shows that the HD-ND nanoaggregates sizes ranging from 5 - 50 nm obtained by the milling treatment of commercial ND powders are randomly and individually located on the graphene surface. The original structure of ND is kept well after depositing on the graphene support as displayed the HRTEM image in Fig. 3D. The TEM images of the HD-ND/graphene catalysts with 12 wt% and 30 wt% ND are also presented in Fig. S2 and Fig. S3. It can be seen that parts of the HD-NDs are seriously reaggregated in the 12 wt% catalyst. However, as to the 30 wt% catalyst, it is hard to find the separate HD-ND nanoaggregates on the graphene surface, only a thick ND layer can be observed (Fig. S3A and Fig. S3B), in agreement well with the SEM results (Fig. 2C and Fig. 2D). The SEM and TEM results provide abundant evidence that the HD-ND nanoaggregates can be evenly and separately distributed on the graphene support when the ND weight loading is around 4 wt%.

The XRD patterns of the commercial ND powders, the HD-ND/graphene catalyst (4 wt%) and the pure graphene are shown in Fig. S4. The peaks at 43.8° and 75.4° are ascribed to the (111) and (220) diffraction planes of pure commercial ND powders. The broaden peak at 26.5° corresponds to the (002) diffraction of graphite crystal plane. From the XRD results, we can conclude that the HD-ND nanoaggregates are successfully distributed on the few-layer graphene support, consisting well with the SEM and TEM observations. Raman spectra of few-layer graphene and HD-ND/Graphene catalysts are displayed in Fig. S5. For the pure few-layer graphene support, the strong D band and G band are observed. The Raman quantitative results of graphene give the I_D/I_G value around 2.4. After locating HD-ND nanoaggregates onto the few-layer graphene support, the strong Raman bands in the HD-ND/graphene catalyst are still observed and the deconvolution results give a 2.7 I_D/I_G value, revealing a slight disturbance occurred on the graphene surface after the deposition of HD-ND nanoaggregates.

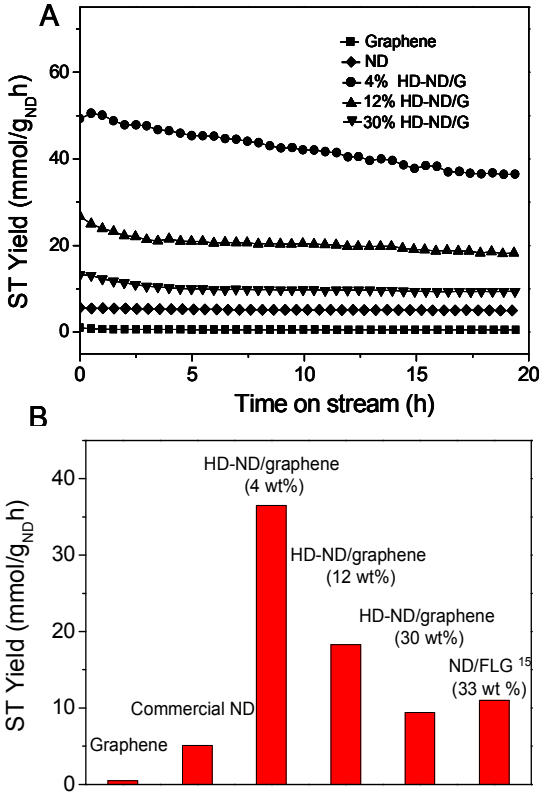


Fig. 4 A) Catalytic performance over few-layer graphene, HD-ND/graphene catalysts with different ND weight loading (4 wt%, 12 wt%, 30 wt%) and commercial ND powders. B) Styrene specific rate of carbon-based catalysts under steady state. Reaction conditions: T = 550 °C, Flow rate = 10 ml min^{-1}, 2.6% ethylbenzene with He balance.

In order to evaluate the catalytic performance of the HD-ND/graphene catalysts in the dehydrogenation of ethylbenzene, 50 mg of the as-prepared catalysts are placed at the center of a quartz reactor. The reaction is carried out at 550 °C under atmospheric pressure conditions similar to those reported by our previous work.[7, 8] The reaction rate is expressed as the amount of styrene produced per gram of catalyst per hour (mmol ST g^{-1} h^{-1}). The catalyst selectivity to styrene has also been investigated. The catalytic performances of the few-layer graphene, HD-ND/graphene catalysts with different ND weight loading (4 wt%, 12 wt%, 30 wt%) and commercial ND powders along with reaction time are shown in Fig. 4 and Fig. S6. The carbon balance under the present conditions is nearly 100%. It can be noted that the ST yield over pure few-layer graphene catalyst is just 0.5 mmol ST g^{-1} h^{-1} after 20 h test (Fig. 4A), and the selectivity of ST finally stabilizes at 88.9% (Fig. S6). However, for the HD-ND/graphene catalysts with the different ND weight loadings, the 4 wt% catalyst with a 36.5 mmol ST g_{ND}^{-1} h^{-1} ST yield is observed, which is much higher than those of 12 wt% (18.3 mmol ST g_{ND}^{-1} h^{-1}) and 30 wt% (9.4 mmol ST g_{ND}^{-1} h^{-1}) HD-ND/graphene catalysts and commercial ND powders (5.1 mmol ST g_{ND}^{-1} h^{-1}) as presented in Fig. 4A. Even after 60 h test, the ST yield over HD-ND/graphene (4 wt%) was still stabilized at 34.2 mmol ST g_{ND}^{-1} h^{-1} as shown in Fig. S7. It has to be mentioned that the ST yield of the as-prepared 4 wt% HD-ND/graphene catalyst is higher than that of 33 wt% ND/FLG composite (11.0 mmol ST g_{ND}^{-1} h^{-1}) reported by Pham-Huu et al.[14, 15] The selectivity of ST (Fig. S6) over all the HD-ND/graphene catalysts is higher than that of commercial ND powders and pure few-layer graphene. The dehydrogenation activity expressed per weight of ND obtained over the HD-ND/graphene catalysts (4 wt%) is significantly improved comparing with the commercial ND powders. This can be attributed to the highly dispersed ND nanoaggregates on the graphene surface providing a relatively higher density of active sites for the dehydrogenation reaction. In addition, the three dimensional few-layer graphene support can be benefit for the heat and mass transfer during the dehydrogenation reaction, which can also promote the ST selectivity. However, we can still note that the ST yields of the 12 wt% and 30 wt% HD-ND/graphene catalysts are lower than that of the 4 wt% HD-ND/graphene catalyst, probably due to the reaggregation of HD-ND in the higher ND loading catalysts, which is also proved by the SEM (Fig. 2C and 2D) and TEM results (Fig. S2 and Fig. S3).

In summary, we have successfully demonstrated the novel HD-ND nanoaggregates supported on graphene as robust metal free catalysts for the ethylbenzene direct dehydrogenation reaction to styrene. The HD-ND nanoaggregates sizes ranging from 5-50 nm are facilely obtained by the traditional milling treatment of commercial ND powders. The as-prepared highly dispersed ND nanoaggregates are evenly and separately located on the graphene support, providing a relatively higher density of active sites for the dehydrogenation reaction. The HD-ND/graphene catalyst shows robust catalytic activity in dehydrogenation of ethylbenzene to styrene, comparing with that of the commercial ND powders and pure graphene support. In addition, it is found that ST yield over the HD-ND/graphene catalyst with 4 wt% ND loading is 36.5 mmol ST g_{ND}^{-1} h^{-1}, which is much higher than that of 12 wt%, 30 wt% HD-ND/graphene catalysts and even the previous reported ND catalyst (33 wt% ND/FLG composite with 11.0 mmol ST g_{ND}^{-1} h^{-1}), displaying its potential application as a metal free catalyst in gaseous catalytic reactions.

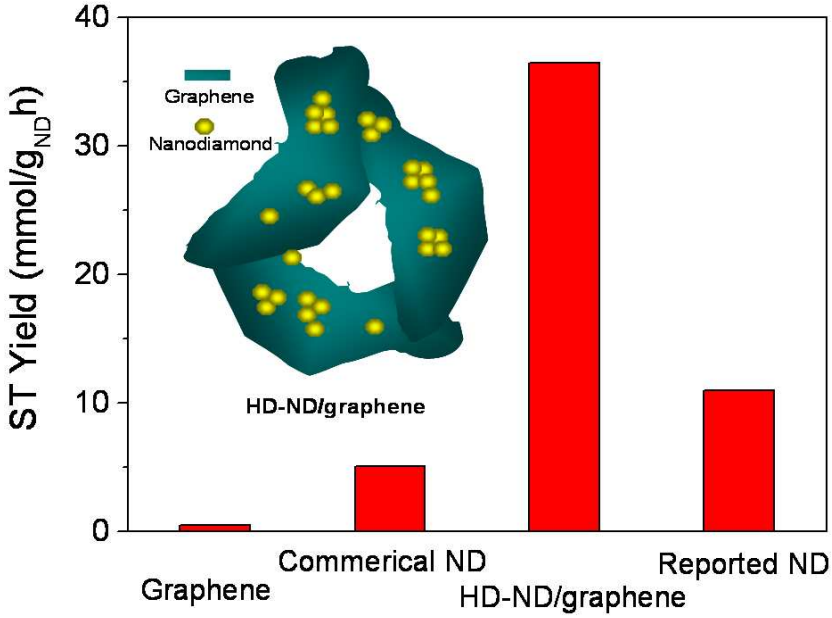
We would like to acknowledge the financial support by the National Natural Science Foundation of China (No. 21203214,

21133010, 21261160487, 21473223, 21573254), the National Basic Research Program (973 Program, No. 2011CBA00504), the Institute of Metal Research, Youth Innovation Promotion Association (CAS), the Sinopec China and the Strategic Priority Research Program of the Chinese Academy of Sciences, Grant No. XDA09030103.

Notes and references

1 A. Krueger, *J. Mater. Chem.* 2011, **21**, 12571.
2 S. J. Yu, M. W. Kang, H. C. Chang and Y. C. Yu, *J. Am. Chem. Soc.*, 2005, **127**, 17604.
3 K. Y. Niu, H. M. Zheng, J. Sun and X. W. Du, *Angew. Chem. Int. Ed.*, 2011, **50**, 4099.
4 Y. R. Chang, et al., *Nat. Nanotechnol.*, 2008, **3**, 284.
5 K. D. Behler, *ACS Nano*, 2009, **3**, 363.
6 A. Krueger, *Adv. Mater.* 2008, **20**, 2445.
7 J. Zhang and D. S. Su, *Angew. Chem. Int. Ed.*, 2010, **49**, 8640.
8 H. Y. Liu, J. Y. Diao, D. S. Su, *Chem. Commun.*, 2014, **50**, 7810.
9 V. Y. Dolmatov, *Russ. Chem. Rev.*, 2001, **70**, 607.
10 A. Krueger, *Adv. Mater.*, 2008, **20**, 2445.
11 J. J. Delgado, R. Vieira, G. Rebmann and D. S. Su, *Carbon*, 2006, **44**, 799.
12 G. Wine, J. P. Tessonnier, C. Pham-Huu and M. J. Ledoux, *Chem. Commun.*, 2002, **20** ,2418.
13 H. Yuan, H. Y. Liu and D. S. Su, *ChemCatChem*, 2013, **5**, 1713.
14 (a) T. Tran Thanh, H. Ba, C. Pham-Huu, *J. Mater. Chem. A*, 2014, **2**, 11349; (b) Z. Zhao and Y. Dai, *J. Mater. Chem. A*, 2014, **2**, 13442.
15 H. Ba, Y.F Liu, C. Pham-Huu, *Catal. Today*, 2015, **249**, 167.
16 X. Wang, G. Q. Shi, *Energy Environ. Sci.*, 2015, **8**, 790.
17 J. Y. Diao, H. Y. Liu, D. S. Su, *Chem. Commun.*,2015, **51**, 3423
18 B. Machado and P. Serp, *Catal. Sci. Technol.*, 2012, **2**, 54.
19 Y. Cheng, Y. Fan, M. Qiao, *Catal. Sci. Technol.*, 2015, **5**, 3903.
20 X. Liu, Y. Sui, T. Duan, Y. Han, *Catal. Sci. Technol.*, 2015, 5, 1658.
21 A. Kruger and E. Osawa, *Carbon*, 2005, **43**, 1722.

Table of Contents



Highly dispersed nanodiamonds (HD-NDs) supported on few-layer graphene (HD-ND/graphene) are successfully prepared for the ethylbenzene dehydrogenation to styrene. The as-prepared HD-ND/graphene catalyst presents higher catalytic performance than that of few-layer graphene and commercial ND powders, showing its potential application in chemical industry.