Catalysis Science & Technology

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/catalysis

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Graphene oxide: an effective acid catalyst for the synthesis of polyoxymethylene dimethyl ethers from methanol and trioxymethylene†

Ruiyi Wang,[a,b] Zhiwei Wu,[a] Zhangfeng Qin,*[a] Chengmeng Chen,[a] Huaqing Zhu,[a] Jianbing Wu,[a,b] Gang Chen,[b] Weibin Fan[a] and Jianguo Wang*[a]

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

Graphene oxide (GO) prepared by a modified Hummers' method exhibits excellent catalytic performance in the synthesis of polyoxymethylene dimethyl ethers (PODE$_n$) from methanol (MeOH) and trioxymethylene (TOM), owing to a synergy between the sulfonic groups and the hydroxyl and carboxyl groups present on the surface of GO with unique layered structure.

Polyoxymethylene dimethyl ethers (PODE$_n$) are a kind of ether compounds with the formula $CH_3O(CH_2O)_nCH_3$ ($n > 1$). As a promising diesel additive, PODE$_n$ is very effective in improving the efficiency of combustion and reducing the emission of NO$_x$ and powderous pollutants.[1–3] As a result, the synthesis of PODE$_n$ from methanol (MeOH) and methanol derivatives such as trioxymethylene (TOM) and dimethoxymethane (DMM), which can extend the methanol industry chain and digest the large surplus production capacity of methanol, has attracted extensive attention in recent years.[4–6]

The synthesis of PODE$_n$ is considered as an acid catalyzed reaction and various liquid and solid acids have been used in the synthesis of PODE$_n$. PODE$_n$ is primitively obtained from methanol and formaldehyde (FA) or polyformaldehydes (PF$_n$) catalyzed by H_2SO_4 or CF_3SO_3H;[7] from PF$_n$ and methanol over the CF_3SO_3H catalyst, the mass yield of PODE$_{1–5}$ was 86.6% at 115 °C. With various ionic liquids as the catalysts and methanol and TOM as the reactants, Chen and coworkers reported that the mass yield of PODE$_{2–8}$ reached 73.3% at 115 °C, with a TOM conversion of 90.1%.[8]

Meanwhile, various solid acids including ion exchange resins,[9–11] PVP-stabilized heteropolyacids,[12] and zeolites[4,5] were also used as the catalysts in the synthesis of PODE$_n$, exhibiting great advantages over the liquid acids in many aspects like in reducing equipment corrosion and facilitating product separation. By reacting DMM with TOM over CT175 resin, Wang and coworkers reported that the conversion of TOM and the selectivity to PODE$_{3–8}$ at 90 °C reached 89.0% and 64.2%, respectively.[9] Zhao and coworkers used MCM-22 zeolite as catalyst and MeOH and TOM as raw materials to synthesize PODE$_n$; the selectivity to PODE$_{3–8}$ reached 29% at 120 °C.[4] Subsequently, Wu and coworkers found that HZSM-5 zeolite of high Si/Al ratio is catalytically effective in the synthesis of PODE$_n$ from DMM and TOM; over HZSM-5 with a Si/Al molar ratio of 580, the mass selectivity to PODE$_{2–8}$ reached 88.5% with a TOM conversion of 85.3%, after reaction for 45 min at 120 °C with a feed DMM/TOM molar ratio of 2.[5] In general, the activity of a solid acid catalyst and the product distribution in the PODE$_n$ synthesis are closely related to its textural property and surface acidity;[5,13,14] proper pore structure and medium-strong Brönsted acid sites are conducive to the PODE$_n$ synthesis.

However, it is some unusual that carbon materials are rarely used as a catalyst in the PODE$_n$ synthesis, though they are often provided with or easily functionalized with abundant acidic groups. Especially, graphene and graphene based materials have aroused great interests of researchers in catalysis, owning to their unique properties such as large surface area, high electronic conductivity and thermal stability. When incorporated with other components such as metallic nanoparticles,[15, 16] polymers,[17] and metal oxide,[18] these graphene hybrids exhibited impressive catalytic performance in various reactions. As a matter of fact, graphene and its derivatives, such as graphene oxide (GO), reduced GO and doped graphene, are also catalytically active in many processes due to the presence of a variety of surface heteroatoms or oxygen-containing functionalities.[19 – 22] As reported by Dreyer and coworkers,[23] GO may bear several types of oxygenated functional groups such as carboxyl, hydroxyl, carbonyl and sulfonyl groups and can then be an effective carbocatalyst for many reactions such as the oxidation of alcohols and hydration of alkynes. Recently, Zhang and coworkers demonstrated that GO as a catalyst was active in the selective hydrolysis of cellulose to glucose.[24] In Wang and coworkers' research, GO was used as a green and efficient carbocatalyst for the fructose dehydration to 5-hydroxymethylfurfural.[25] Zhu and coworkers also proved that GO was a highly active, selective and reusable solid-acid catalyst for the production of alkyl levulinates via alcoholysis or esterification.[26] Taking account of the large surface area, unique layered structure and abundant surface acid groups for GO, there is an optimistic expectation for the performance of GO as a metal free acid carbocatalyst in the PODE$_n$ synthesis.

In this work, therefore, GO was used as an acid carbocatalyst in the synthesis of PODE$_n$ from MeOH and TOM; to reveal the catalytic role of various oxygenated functional groups on the GO surface, the catalytic reactions over GO with selectively preserved groups were comparatively investigated.

GO was prepared by a modified Hummers' method,[27] followed by exfoliation in aqueous solution under sonicating for 2 h (ESI†). The atomic force microscope (AFM) and scanning electron microscope (SEM) characterizations indicate that as-prepared GO is in flimsy sheets with a thickness of 1.42 nm (Figs. S1 and S2, ESI†). According to the elemental analysis, the mass fractions of C, O, S, H and N elements are 47.98%, 47.52%, 2.36%, 2.02%, and 0.12%, respectively (Table S1, ESI†); the heteroatoms, especially O, S and H, constitute the various acid groups. The XRD pattern of GO displays an intense peak at 12.56° typical for C (001), suggesting that the interlayer space is expanded from 0.338 nm of graphite to 0.704 nm of GO because of the insertion of various oxygen-containing functional groups (Fig. S3, ESI†).

The catalytic performance of GO in the synthesis of $PODE_n$ was tested in a stainless steel autoclave of 100 mL lined with Teflon (ESI†). A series of preliminary tests (Table S2, ESI†) illustrate that a temperature of 120 °C, a reaction time of 10 h and a GO catalyst amount of 5 wt.% are probably the optimal reaction conditions for the synthesis of $PODE_n$ from MeOH and TOM; under such conditions, the conversion of TOM and the mass selectivity to $PODE_{2-8}$ reach 92.8% and 30.9%, respectively. Interestingly, a high selectivity to $PODE_{2-8}$ is generally accompanied with a relative high selectivity to FA, which may prove that the dissociation of trioxymethylene rate is a crucial step in the process of $PODE_n$ synthesis, in accord with the results of Wu, Li, and coworkers.[5,14]

To ascertain that the synthesis of $PODE_n$ is heterogeneously catalyzed by GO rather than by the acid species leached from GO, GO was filtered from the reaction mixture after the reaction was carried out under the optimal conditions for 0.5 h, leaving the remaining solution to continue the reaction under stirring at 120 °C for another 10 h. As given in Table 1, in comparison with those obtained just before the removal of GO (Entry 1), the conversions of TOM and MeOH only have a tiny increment after reaction for 10 h in the absence of GO catalyst (Entry 2). As a result, the catalytic contribution of the acid species in the reaction mixture leached from GO surface to $PODE_n$ synthesis can then be excluded.

Table 1 Reactant conversion and product selectivity for the synthesis of $PODE_n$ from MeOH and TOM over various catalysts[a]

Entry	Catalyst	Conversion (%)		Mass selectivity (%)			
		MeOH	TOM	DMM	$PODE_{2-8}$	MF	FA
1	GO, 0.5 h[b]	48.4	40.2	94.3	0.0	0.0	5.7
2	leaching species[b]	52.2	43.6	94.0	6.0	0.0	0.0
3	GO, 10 h	90.3	92.8	21.1	30.9	0.2	47.8
4	GO-COOH[c]	79.9	71.2	57.5	9.9	0.0	38.6
5	GO-OH[c]	74.0	75.3	68.1	8.9	0.0	23.0
6	GO-HT[c]	37.7	41.9	58.8	6.7	0.0	34.6
7	1,4-dihydroxybenzene	7.2	14.0	80.8	0.0	0.0	19.2
8	1,4-benzoquinone	4.0	11.7	83.7	0.0	0.0	16.3
9	1,4-dicarboxybenzene	11.1	29.1	92.6	0.0	0.0	7.4
10	o-hydroxybenzoic acid	15.4	16.5	96.2	0.0	0.0	3.8
11	phenylsulfonic acid	24.3	51.9	33.2	5.7	9.4	51.7
12	sulfosalicylic acid	52.3	68.4	33.9	10.9	9.5	47.7
13	sulfuric acid[d]	64.2	72.2	29.2	19.3	0.9	50.6
14	S-AC[e]	43.4	38.9	82.5	9.4	0.0	8.1
15	S-CNTs[e]	43.8	41.3	78.3	12.3	0.0	9.4

[a] The reactions were carried out at 120 °C for 10 h, with a catalyst amount of 5 wt.% and initial MeOH/TOM molar ratio of 2. The mass selectivity to a given product is defined as its weight divided by the weight of all products.

[b] GO was filtered from the reaction mixture after the reaction was conducted for 0.5 h, leaving the remaining solution to continue the reaction at 120 °C for another 10 h.

[c] In GO-COOH, the hydroxyl groups on GO were selectively poisoned through siylation with tetramethoxysilane; in GO-OH, the carbonyl and carboxyl groups on GO were selectively removed by reduction with $NaBH_4$; GO-HT, desulfurated GO, is obtained by hydrothermal treatment of GO at 150 °C for 12 h, in which 84.7% of SO_3H groups was removed.

[d] The amount of sulfuric acid is about 0.27 wt.%, equivalent to the same sulfuric content when using 5 wt.% GO as the catalyst.

[e] S-AC and S-CNTs are sulfonated active carbon (AC) and carbon nanotubes (CNTs), respectively, treated in concentrated sulfuric acid at 150 °C for 6 h.

To further understand the catalytic roles of various oxygenated functional groups on the GO surface in $PODE_n$ synthesis, GO catalysts selectively preserved with certain groups were prepared (ESI†). By siylation with tetramethoxysilane, the hydroxyl groups were selectively poisoned;[28] the resultant material is referred to as GO-COOH. Through reduction with $NaBH_4$, the carbonyl and carboxyl groups on GO were selectively removed;[29] the resultant catalyst is denoted as GO-OH. Similarly, 84.7% of the SO_3H groups in GO were removed by hydrothermal treatment at 150 °C for 12 h and the desulfurated GO is then expressed as GO-HT. The preservation of given functional groups is well proved by the elemental analysis, XRD, Raman, FT-IR and XPS spectra, as illustrated in Table S1 and Figs. 3–6, ESI†.

When the hydroxyl and carboxyl groups are selectively poisoned or removed, as given in Table 1, GO-COOH and GO-OH exhibit much lower activity and selectivity to $PODE_{2-8}$ than GO under the same reaction conditions (Entries 4 and 5). The conversions of TOM over GO-COOH and GO-OH are decreased to 71.2% and 75.3%, respectively, from 92.8% over GO (Entry 3). Meanwhile, the selectivities to $PODE_{2-8}$ over GO-COOH and GO-OH are reduced from 30.9% over GO to 9.9% and 8.9%, respectively; DMM turns out to be the primary product. Similarly, over the desulfurated GO-HT, in which most of the sulfonyl groups are removed, the conversion of TOM and selectivity to $PODE_{2-8}$ are also greatly reduced, only 41.9% and 6.7%, respectively (Entry 6). All these suggest that both the sulfonic groups and the hydroxyl and carboxyl groups contribute to the catalytic action of GO on PODE$_n$ synthesis.

A series of model compounds including 1,4-dihydroxybenzene, 1,4-benzoquinone, 1,4-dicarboxybenzene, o-hydroxybenzoic acid, phenylsulfonic acid, sulfosalicylic acid and sulfuric acid are used to mimic various oxygenated functional groups on the carbocatalyst,[30] to explain their catalytic effect on PODE$_n$ synthesis, as also given in Table 1. 1,4-dihydroxybenzene, 1,4-benzoquinone, 1,4-dicarboxybenzene and o-hydroxybenzoic acid show very low catalytic activity in PODE$_n$ syntheis; the conversions of TOM over them are 14.0%, 11.7%, 29.1% and 16.5%, respectively, with DMM as the dominant product (Entries 7–10). Meanwhile, phenylsulfonic acid and sulfosalicylic acid as the catalyst give much higher TOM conversions, 51.9% and 68.4%, respectively (Entries 11 and 12); over them, the mass selectivities to PODE$_{2–8}$ are 5.7% and 10.9%, respectively. It should be noted that sulphuric acid is much more active for the PODE$_n$ synthesis; the conversion of TOM and selectivity to PODE$_{2–8}$ reach 72.2% and 19.3%, respectively, when 0.27 wt.% sulphuric acid (corresponding to the same sulfuric amount as that in 5 wt.% GO) is used (Entry 13). Such a result proves that the carboxyl, hydroxyl and carbonyl groups are catalytically active for the dissociation of TOM and the formation of DMM from FA and MeOH; however, their acidity is probably insufficient for the chain propagation to form PODE$_{2–8}$. The formation of long chain PODE$_{2–8}$ products can be effectively catalyzed by the sulfonic groups.

The catalytic performance of other sulfonated carbon materials in PODE$_n$ synthesis were also tested under the same conditions. As also given in Table 1, the conversions of TOM over sulfonated active carbon and carbon nanotubes (S-AC and S-CNTs, treated in concentrated sulphuric acid at 150 °C for 6 h) are only 38.9% and 41.3% (Entries 14 and 15), respectively, which are much lower than that over GO and even lower than those over GO-OH and GO-COOH. Although GO may have the similar acidic oxygen-containing groups as S-AC and S-CNTs, the catalytic performance of GO is far superior to that of later two sulfonated carbon materials, which should be related to its unique layered structure. The GO sheets possess abundant oxygenated functional groups with armchair and zigzag edges of huge open π-electron environment. The excellent catalytic performance of GO in the synthesis of PODE$_n$ from MeOH and TOM may then be ascribed to a synergy between the sulfonic groups and the hydroxyl and carboxyl groups present on the surface GO with unique layered structure.

On the basis of above observations, possible reaction routes for the synthesis of PODE$_n$ from MeOH and TOM are proposed in Fig. 1. The synthesis of PODE$_n$ involves a series of reactions such as TOM dissociation to FA, condensation of FA with MeOH to DMM, PODE$_n$ chain propagation, Tishchenko reaction of FA to MF and so on. TOM is firstly dissociated to FA and PODE$_n$ is then formed through two sorts of reactions, viz., the chain propagation by reacting hemiformals ($CH_3(OCH_2)_nOH$) with FA and sealing hemiformals with MeOH. Meanwhile, the reverse reactions such as the hydrolysis and dissociation of PODE$_n$ as well as certain side reactions such as Tishchenko reaction forming MF may also occur under the similar conditions. The progress of PODE$_n$ formation is related to the properties of acid sites and reaction environment. A temperature below 120 °C is probably inadequate for the TOM dissociation and PODE$_n$ chain propagation, whereas a temperature above 120 °C may promote the PODE$_n$ dissociation and other side reactions. The formation of DMM is relatively easier, which can be catalyzed by the hydroxyl and carboxyl groups on GO, whereas the formation of hemiformals and the chain propagation may require stronger acid sites like sulfonic groups on GO, in accordance with those observed by Wu, Li, Cao, Wang and coworkers.[5,14,31,32] GO bearing abundant acid hydroxyl and carboxyl groups and sulfonic groups may provide an ideal catalytic environment for the synthesis of PODE$_n$ from MeOH and TOM.

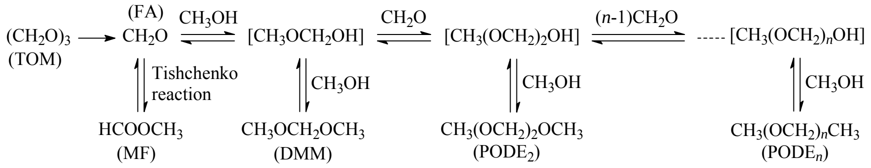


Fig. 1 Proposed reaction routes for the synthesis of PODEn from MeOH and TOM.

The effects of various solvents and raw reactants on the synthesis of PODE$_n$ were also considered, as shown in Table S3, ESI†. When MeOH and TOM are used as the raw materials to synthesize PODE$_n$ (Entry 1), water is produced as a by-product, which may promote the hydrolysis of PODE$_n$ and is then prejudicial to the formation of long chain PODE$_n$. As anticipated, water as an additional solvent exhibits a negative effect on production of PODE$_{2–8}$ (Entry 2). On the other hand, when toluene as an inert solvent is used, the reactant conversion is hardly influenced, whereas the selectivity to PODE$_{2–8}$ is moderately enhanced (Entry 3). Toluene as a solvent is effective to extract ethers products, which may prevent them from further hydrolysis and then shift the reaction to long chain PODE$_n$. In fact, when DMM and TOM were used as the raw materials to synthesis PODE$_n$ (Entry 4), the mass selectivity to long chain PODE$_n$ products is largely enhanced, as such a reaction does not produce water; the mass selectivity to PODE$_{2–8}$ reaches 85.9% and even certain longer chain products are also detected. These may confirm that DMM and TOM are more suitable as the raw materials to get high quality PODE$_n$.[5]

Meanwhile, when MeOH is taken as the sole reactant, GO is rather catalytically inactive and only 2% of it is converted to MF (Entry 5, Table S3, ESI†). On the other hand, when

TOM is used as the sole reactant, its conversion and the selectivity to FA reach 55.6% and 97.0%, respectively, whereas the mass selectivity to MF is only 3% (Entry 6). These further prove that GO as a catalyst is very effective for the dissociation of TOM to FA and further chain propagation with DMM and MeOH to form PODE$_{2–8}$, whereas it is less active for the methanol oxidation and Tishchenko reaction to form the side products such as MF.

The oxygen-containing functionalities on GO surface may not only act as the active sites in the PODE$_n$ synthesis but also serve as surfactants to stabilize the GO suspension, which increases the contacting probability between GO and reactants and enhance the reaction activity (Fig. S7, ESI†). However, GO as a heterogeneous catalyst is easily separated from the suspension mixture by simple filtration. To test the catalytic stability and reusability of GO in PODE$_n$ synthesis, GO was separated from the mixture after reaction by filtration and used for the next run without any further treatment. As illustrated in Fig. S8, ESI†, GO as the catalyst is deactivated slightly after being reused for five cycles; the conversion of TOM is decreased from 92.8% to 85.2%, whilst the mass selectivity to PODE$_{2–8}$ is also decreased from 30.9% to 16.3%. Such impairment should be attributed to the slow elimination of hydroxyl groups under the harsh hydrothermal reaction conditions.[25,26] Liao and coworkers also reported that GO could be reduced to single-layer graphene in water at 95 °C.[33] Fortunately, the oxygen-containing functionalities served as the active sites can be easily refurnished with concentrated sulphuric acid. As displayed in Fig. S8, ESI†, when the deactivated GO is treated in the concentrated sulphuric acid at 80 °C for 4 h, the conversion of TOM and the mass selectivity to PODE$_{2–8}$ are reclaimed to 89.5% and 30.6%, respectively.

In conclusion, GO as a catalyst performs excellently in the synthesis of PODE$_n$ from MeOH and TOM, comparable with other catalysts previously reported at relatively low temperature (Table S4, ESI†).[4,5,9,31] GO is catalytically very effective for the dissociation of TOM to FA and further chain propagation with DMM and MeOH to form PODE$_{2–8}$, whereas it is less active for the methanol oxidation and Tishchenko reaction to form the side products such as MF. The excellent catalytic performance of GO should be ascribed to a synergy between the acid sulfonic groups and the hydroxyl and carboxyl groups present on the surface of GO with unique layered structure. Such results suggest that GO can be a potential catalyst for the synthesis of PODE$_n$, which are also meaningful for the extension of GO application in other catalytic synthesis processes.

The authors are grateful for the financial support of the National Natural Science Foundation of China (21227002, 21403268, 21573270).

Notes and references

[a] *State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, P.O. Box 165, Taiyuan, Shanxi 030001, PR China. E-mail: qzhf@sxicc.ac.cn (Z. Qin); iccjgw@sxicc.ac.cn (J. Wang); Fax: +86-351-4041153; Tel: +86-351-4046092*
[b] *University of Chinese Academy of Sciences, Beijing 100049, PR China*
[c] *Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi 030001, PR China*

† Electronic Supplementary Information (ESI) available: More experimental details and catalyst characterization and reaction test results. See DOI: 10.1039/b000000x/

1 N. Schmitz, F. Homberg, J. Berje, J. Burger and H. Hasse, *Ind. Eng. Chem. Res.*, 2015, **54**, 6409–6417.
2 Y. Zhao, Z. Xu, H. Chen, Y. Fu and J. Shen, *J. Energ. Chem.*, 2013, **22**, 833–836.
3 J. Burger, M. Siegert, E. Ströfer and H. Hasse, *Fuel*, 2010, **89**, 3315–3319.
4 Q. Zhao, H. Wang, Z. Qin , Z. Wu, W. Fan and J. Wang, *J. Fuel Chem. Technol.*, 2011, **39**, 918–923.
5 J. Wu, H. Zhu, Z. Wu, Z. Qin, L. Yan, B. Du, W. Fan and J. Wang, *Green Chem.*, 2015, **17**, 2353–2357.
6 J. Wu, Z. Wu, R. Wang, R. Shi, Z. Qin, H. Zhu, M. Dong, W. Fan and J. Wang, *J. Fuel Chem. Technol.*, 2015, **43**, 816–828.
7 P. Renata, EP Pat., 1505049A1, 2005.
8 J. Chen, Z. Tan, C. Xia, X. Zhang and Z. Li, US Pat., 7560599B2, 2009.
9 L. Wang, W. Wu, T. Chen, Q. Chen and M. He, *Chem. Eng. Commun.*, 2014, **201**, 709–717.
10 M. Arvidson, M. E. Fakley and M. S. Spencer, *J. Mol. Catal.*, 1987, **41**, 391–393.
11 Y. Zheng, Q. Tang, T. Wang, Y. Liao and J. Wang, *Chem. Eng. Technol.*, 2013, **36**, 1951–1956.
12 X. Fang, J. Chen, L. Ye, H. Lin and Y. Yuan, *Sci. China Chem.*, 2015, **58**, 131–138.
13 W. Fu, X. Liang, H. Zhang, Y. Wang and M. He, *Chem. Commun.*, 2015, **51**, 1449–1452.
14 H. Li, H. Song, L. Chen and C. Xia, *Appl. Catal. B*, 2015, **165**, 466–476.
15 G. Wu, X. Wang, N. Guan and L. Li, *Appl. Catal. B*, 2013, **136–137**, 177–185.
16 R. Wang, Z. Wu, C. Chen, Z. Qin, H. Zhu, G. Wang, H. Wang, C. Wu, W. Dong, W. Fan and J. Wang, *Chem. Commun.*, 2013, **49**, 8250–8252.
17 J. Vickery, A. Patil and S. Mann, *Adv. Mater.*, 2009, **21**, 2180–2184.
18 Z. Zhang, F. Xiao, Y. Guo, S. Wang and Y. Liu, *ACS Appl. Mater. Interfaces*, 2013, **5**, 2227–2233.
19 J. Long, X. Xie, J. Xu, Q. Gu, L. Chen and X. Wang, *ACS Catal.*, 2012, **2**, 622–631.
20 F. Zhang, H. Jiang, X. Li, X. Wu and H. Li, *ACS Catal.*, 2014, **4**, 394–401.
21 Y. Song, K. Qu, C. Zhao, J. Ren and X. Qu, *Adv. Mater.*, 2010, **22**, 2206–2210.
22 A. Dhakshinamoorthy, M. Alvaro, P. Concepcion, V. Fornes and H. Garcia, *Chem. Commun.*, 2012, **48**, 5443–5445.
23 D. Dreyer, H. Jia and C. Bielawski, *Angew. Chem. Int. Ed.*, 2010, **49**, 6813–6816.
24 X. Zhao, J. Wang, C. Chen, Y. Huang, A. Wang and T. Zhang, *Chem. Commun.*, 2014, **50**, 3439–3442.
25 H. Wang, Q. Kong, Y. Wang, T. Deng, C. Chen, X. Hou and Y. Zhu, *ChemCatChem*, 2014, **6**, 728–732.
26 S. Zhu, C. Chen, Y. Xue, J. Wu, J. Wang and W. Fan, *ChemCatChem*, 2014, **6**, 3080–3083.
27 C. Chen, Q. Zhang, M. Yang, C. Huang, Y. Yang and M. Wang, *Carbon*, 2012, **50**, 3572–3584.
28 H. Yao, L. Jin, H. Sue, Y. Sumi and R. Nishimura, *J. Mater. Chem. A*, 2013, **1**, 10783–10789.
29 H. Shin, K. Kim, A. Benayad, S. Yoon, H. Park, I. Jung, M. Jin, H. Jeong, J. Kim, J. Choi and Y. Lee, *Adv. Function. Mater.*, 2009, **19**, 1987–1992.
30 S. Wu, G. Wen, X. Liu, B. Zhong and D. Su, *ChemCatChem*, 2014, **6**, 1558–1561.
31 J. Cao, H. Zhu, H. Wang, L. Huang, Z. Qin, W. Fan and J. Wang, *J. Fuel Chem. Techno.*, 2014, **42**, 986–993.
32 F. Wang, G. Zhu, Z. Li, F. Zhao, C. Xia and J. Chen, *J. Mol. Catal. A*, 2015, **408**, 228–236.
33 K. Liao, A. Mittal, S. Bose, C. Leighton, K. Mkhoyan and C. Macosko, *ACS nano*, 2011, **5**, 1253–1258.

Graphic Abstract

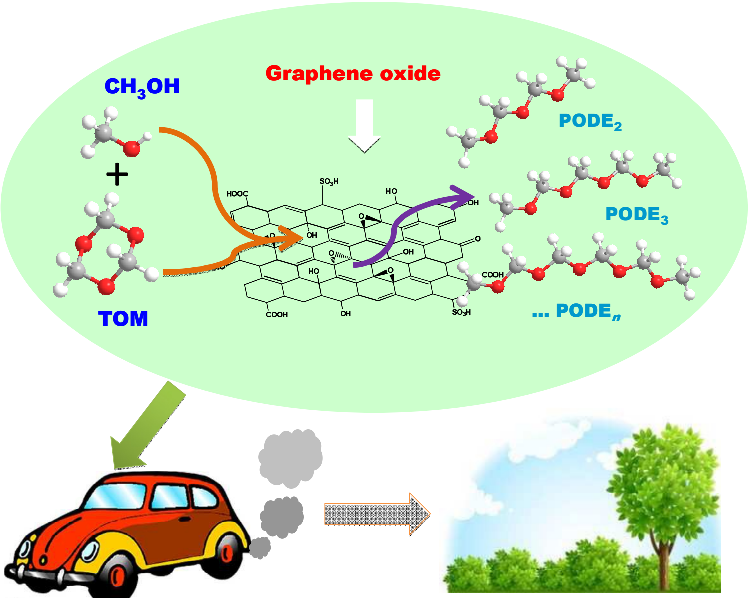
Graphene oxide: an effective acid catalyst for the synthesis of polyoxymethylene dimethyl ethers from methanol and trioxymethylene

Ruiyi Wang,[a,b] Zhiwei Wu,[a] Zhangfeng Qin,*[a] Chengmeng Chen,[a] Huaqing Zhu,[a] Jianbing Wu,[a,b] Gang Chen,[b] Weibin Fan[a] and Jianguo Wang*[a]

[a] *State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, P.O. Box 165, Taiyuan, Shanxi 030001, PR China. E-mail: qzhf@sxicc.ac.cn (Z. Qin); iccjgw@sxicc.ac.cn (J. Wang); Fax: +86-351-4041153; Tel: +86-351-4046092*

[b] *University of Chinese Academy of Sciences, Beijing 100049, PR China*

[c] *Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi 030001, PR China*



Graphene oxide as an acid carbocatalyst performs excellently in the synthesis of polyoxymethylene dimethyl ethers from methanol and trioxymethylene.