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Graphene-Promoted Acetalisation of Glycerol under Acid-Free Conditions

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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Serendipity led us to unveil unexpected and uncovered properties of graphene for the acetalisation of glycerol with both aldehydes and ketones, furnishing an acid-free process for fuel bio-additive candidates. Mechanistic studies ruled out the intervention of residual acidic species or metallic cations at the surface of graphene, and therefore, the peculiar electronic properties of graphene are most probably responsible of this unforeseen reactivity. Recycling studies revealed the robustness of graphene in the experimental conditions since only a marginal erosion of the reaction yield was observed after six cycles.

1. Introduction

The exhaustion of non-renewable fossil fuel reserves and the rapid climate change induced by the emissions of greenhouse gases have emphasized the urgent need for sustainable technologies.^{1, 2} The transformation of biomass has been recognized as the most promising sustainable technology to provide chemical intermediates, biodiesel and biomaterials.³⁻⁶ The deconstruction of biopolymers and the transformation of biomass feedstocks into small molecules of high-added value have been achieved using acids, bases, enzymes, transition metals as well as supercritical conditions.⁷⁻¹⁶

Glycerol is an abundant low-value chemical, synthesized from propylene oxide or obtained from renewable resources as a byproduct from the saponification of triglycerides in the soap industry and biodiesel production. Although it has recently been considered as a green solvent,¹⁷⁻²¹ glycerol itself has a low interest as chemical or fuel additive since it is a highly hygroscopic and viscous compound that polymerizes at high temperature and oxidizes to hazardous acrolein. By contrast, chemically-modified glycerol derivatives by etherification²² and esterification are excellent candidates for oxygenated fuel additives with anti-freezing, anti-detonant and octane-improving properties.²³ Glycerol acetals have also been used in other valorization strategies as flavors,²⁴ surfactants,²⁵ and low-toxic solvent for both pharmaceutical²⁶ and veterinarian formulations.²⁷

The acetalisation of glycerol is a well-known acid-catalyzed

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reaction. While the use of homogeneous acids (e.g., sulfuric acid, hydrogen chloride, p-toluenesulfonic acid...) can, in some extend, be attractive since they are inexpensive and highly active for the condensation of glycerol with carbonyl compounds,²⁸ extra neutralization steps and both recovery and corrosive issues disgualified them for sustainable processes when high loadings are required. On the other hand, heterogeneous solid acids have shown great potential as recyclable liquid acid surrogates for the transformation of biomass feedstocks, especially for biodiesel production,^{8, 9, 14, 16, 29} but for most of them, the catalytic activity results from non-easily quantifiable contributions, of Brønsted and Lewis acid properties. This, led us to consider graphene (GR) as a non-Lewis acidic platform for heterogeneous sulfonic acids. GR is certainly one of the most exciting material known to date due to its unique properties and is easily functionalized to graphene-based materials³⁰⁻³⁶ that have been extensively used as catalysts for various reactions,³⁷⁻⁴¹ including biomass transformation.⁴² This honeycomb-structured two dimensional material of one-atomic thickness, consisting of sp²-hybridized carbons, presents a high electron mobility (10 000 cm^2 .V⁻¹.s⁻¹), a thermal conductivity of 5 000 W.m⁻¹.K⁻¹, an exceptional mechanical resistance (~1 TPa, 100 times stronger than steel) and a large theoretical surface area of 2630 m².g⁻¹.43-46</sup> In a recent report we described a scalable synthesis of sulfonated graphene (GR-SO₃H) that could find applications in acid-catalyzed transformations.⁴⁷ However, we describe herein how serendipity led to unveil unexpected and uncovered properties of GR that surpass the activity of GR-SO₃H for the acetalisation of glycerol in neutral conditions.

2. Experimental

2.1. Materials

Graphite, glycerol, benzaldehyde, acetone, anisaldehyde, *trans*cinnamaldehyde, furfural, acetophenone, cyclopentanone, cyclohexanone and cellobiose were purchased from Sigma-Aldrich, Fischer Scientific Ltd, Alfa Aesar and TCI Europe companies. All

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ARTICLE

reagents and solvents were used as received without further purification with the exception of furfural which was distilled before use.

2.2. Preparation of graphene (GR)

GR was prepared according to our previously reported procedure.⁴⁷ Graphite powder (2 g) was mixed with sulfuric acid (4.6 wt. equiv., 5 mL), potassium persulfate (0.5 wt. equiv., 1 g) and phosphorus pentoxide (0.5 wt. equiv., 1 g). The resulting mixture was heated at 80 °C for 2 hours. Then, the solid was filtered through a fritted glass and washed with deionized (DI) water (100 mL), MeOH (200 mL) and Et₂O (200 mL). The resulting black paste (2.15 g, 108% in mass) was dried at 40 °C under vacuum overnight. The resulting material (2.15 g) was mixed with sulfuric acid (43.9 wt. equiv., 54 mL) at 0 °C and potassium permanganate (3.5 wt. equiv., 7.46 g) was then added by portion with careful attention. The reaction mixture was stirred at 35 °C for 2 hours and then the reaction mixture was cooled to 0 °C. followed by the addition of 30% hydrogen peroxide (2.84 wt. equiv., 5.9 mL) in DI water (80 mL). The solid was centrifuged (4000 rpm, 20 minutes) and the liquid phase was removed. DI water (3 x 50 mL) was added and the centrifugation (4000 rpm, 15 minutes) was performed three times. The same procedure was carried out with MeOH and Et₂O. The resulting brown solid graphene oxide (GO), 3.54 g, 164% in mass) was dried at 40 °C under vacuum overnight.

GO (500 mg) was sonicated in DI water (500 mL) for 2 hours. A solution of 5% Na₂CO₃ (12 mL) was added in order to increase the pH up to 9-10. Then, 64% hydrazine hydrate (41.2 wt. equiv., 20 mL) was added to the suspension and the mixture was refluxed for 24 hours. The solution was cooled down to room temperature and filtered through Millipore membrane (nylon filter 0.45 μ m, 47 mm) and washed with 1N HCl (100 mL) and acetone (300 mL). GR (black powder, 284 mg, 57% in mass) was dried at 40 °C under vacuum overnight.

2.3. Preparation of sulfonated graphene (GR-SO₃H)

GR (273 mg) was sonicated in DI water (40 mL) for 2 hours. Then, sodium nitrite (3.47 wt. equiv., 947 mg) and sulfanilic acid (2.89 wt. equiv., 789 mg) were added to the resulting solution, allowing the formation of the diazonium salt *in situ*, and the reaction was conducted at 25 °C for 24 hours. The solution was filtered through Millipore membrane (nylon filter 0.45 μ m, 47 mm) and washed with 1N HCl (100 mL) and acetone (300 mL). The black powder (352 mg, GR-SO₃H) was dried at 40 °C under vacuum overnight. The loading of $-SO_3H$ was calculated to be 1.79 mmol SO₃H.g⁻¹ by elemental analysis (C : 64.54%, H : 1.87%, N : 1.84%, S : 5.72%).

2.4. Acetalisation of glycerol

In a typical experiment, GR (25 mg), benzaldehyde (10 mmol) and glycerol (1 mmol) were placed in a sealed tube and stirred at 100 °C for 2 hours. The resulting mixture was filtered through Millipore membrane (nylon filter 0.45 μ m, 47 mm) and the solid was thoroughly washed with acetone. The filtrate was concentrated under *vacuum* and analysed by ¹H NMR using 1,3,5-trimethylbenzene as external standard.

2.5. Recycling studies

Upon completion of the reaction, the catalyst was recovered by filtration, washed with acetone and dried under reduced pressure at 25 °C for 6 hours, prior to its reuse in another run.

2.6. Hydrolysis of cellobiose

Cellobiose (200 mg, 0.58 mmol), GR-SO₃H (20 mg), and deionized water (40 mL) were introduced in a batch-type autoclave (60 mL) equipped with an internal temperature control. The system was purged and pressurized to 20 bar with Ar. The suspension was heated to 150 °C (10 °C.min⁻¹) and agitated using a magnetic stirrer. After reaction and cooling, the catalyst was separated over Millipore membrane (Teflon filter 0.45 μ m, 47 mm) and dried at room temperature overnight. The colorless filtrate was analyzed on a Shimadzu HPLC apparatus (COREGEL 107H column, 0.5 mL.min⁻¹ of 0.001% H₂SO₄, 70 °C, RI detector) for cellobiose and glucose quantification. Yields are molar yields and are calculated as follows: yield (%) = 100 x (n_{glucose}/n_{initialcellobiose}//2.

2.7. Analytical methods

Transmission Electron Microscopy (TEM) was performed on a Hitachi HF2000 (cold field emission gun, accelerating voltage: 100 kV). Scanning Electron Microscopy (SEM) was performed on a JEOL JSH7600F (field emission gun, accelerating voltage: 5 kV, in lens detector of secondary electrons). X-ray photoelectron spectroscopy (XPS) was performed on a ThermoFisher Scientific K-ALPHA spectrometer for disk surface analysis with a monochromatized AlK α source (hv = 1486.6 eV) and a 200 micron spot size. A pressure of 10⁻⁷ Pa was maintained in the chamber during analysis. The full spectra (0-1150eV) were obtained at a constant pass energy of 200eV and high resolution spectra at a constant pass energy of 40 eV. Charge neutralization was required for all insulating samples. High resolution spectra were fitted and quantified using the AVANTAGE software provided by ThermoFisher Scientific. X-Ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-Ray Diffractometer.

3. Results and discussion

3.1. Graphene synthesis

Graphene-based materials used in this study, *i.e.* GR and GR-SO₃H were prepared according to our recently published procedure.⁴⁷ In short, graphite was oxidized in two sequential steps and exfoliated into graphene oxide (GO) which was subsequently reduced to GR by hydrazine and then, functionalized with benzene sulfonic groups to give GR-SO₃H (Scheme 1).



Scheme 1 Preparation of GR and GR-SO₃H.

Although the process cannot be considered as sustainable, one should remain that graphene is used as a catalyst limiting the impact of its synthesis on the whole process.

Transmission electron microscopy (TEM) analyses showed randomly oriented sheets for both graphene materials (*i.e.*, GR and GR-SO₃H) and the high transparency observed was attributed to the successful exfoliation (Fig. 1).



Fig. 1 TEM images of a) GR and b) GR-SO₃H.



Fig. 2 High resolution of C 1s spectra of a) GR and b) GR-SO₃H. Survey scan spectra of c) purified GR.

The acid group density of GR-SO₃H used in this study was determined to be 1.79 mmol H⁺.g⁻¹ using both acid-base titration and NH₃-TPD methods and this value was correlated by the loading of SO₃H calculated by elemental analysis. Surface analyses by X-ray photoelectron spectroscopy (XPS) revealed a low content of oxygenated species and a high level of sp² carbon consistently with the expected honeycomb-structured material (Fig.s 2a-c).

3.2. Acetalisation of glycerol

We carried out our preliminary studies with the acetalisation of glycerol with benzaldehyde at 100 $^{\circ}\mathrm{C}$ in a sealed tube (Table 1).

 Table 1
 Acetalisation of glycerol with benzaldehyde.

HO - OH +						
Entry	Catalyst	Time	Selectivity	Yield		
		(h)	3a/3b	(%) ^b		
1		2	85/15	26		
2	GR-SO₃H	2	33/67	49		
3	GR-SO₃H	14	62/38	92		
4	GR	2	63/37	91		
5	GR	0.5	66/34	68		
6	GR	1	63/37	82		
7	GR	3	64/36	91		
8	GR	14	65/35	91		
9	GO	14	100/0	25		
10	graphite	2	87/13	23		
11	coronene	2	81/19	16		
12	GR ^c	14	79/21	81		

^{*a*} Reaction conditions: glycerol **1** (1 mmol), benzaldehyde **2** (10 mmol) and the catalyst (25 mg) were stirred at 100 °C for the indicated time. ^{*b*} ¹H NMR yield using 1,3,5-trimethylbenzene as internal standard. ^{*c*} Unpurified GR.

While the background reaction, carried out in the absence of catalyst, gave a mixture of five- and six-membered acetals (compounds 3a and 3b respectively) with 26% combined yield (entry 1), the use of GR-SO₃H (3 mol% H^{\dagger}) gave a much improved, but still unsatisfactory yield of 49% (entry 2). In order to evaluate the impact of graphene-grafted sulfonic acid functions on the reaction outcome, we carried out the acetalisation with unfonctionalized graphene. To our great surprise, a very high yield (91%) was obtained for a mixture of five- and six-membered acetals (entry 4). Such a high yield could be reached with GR-SO₃H, but only after 14 hours of stirring (entry 3). Interestingly, with GR-SO₃H the six membered acetal 3b appeared as the kinetically favored isomer being the major product after 2 hours of stirring, but upon extended reaction times, a reversed selectivity in favor of acetal 3a was observed. Incomplete conversions were observed upon reduced reaction times with GR (entries 5-6), while extended stirring times proved to be useless (entries 7-8). Intrigued by this unexpected high reactivity of GR, we reasoned that it could arise from both residual oxygenated and acidic functions remaining at the surface of the material. While the surface analysis by XPS indeed provided evidences for C-O and C=O bonds at 286.8 and 287.8 eV respectively (Fig. 2a), the absence of peak at ~288.5 eV accounting for carboxylic acids combined to the absence of acidic protons as determined by acid-base titration ruled out the presence of acidic functions at the surface of GR. Moreover, GO, which contains many oxygenated and acidic functions, was found inactive for this transformation, even after prolonged reaction times (entry 9). All these results, suggest that the high activity observed for GR cannot be attributed to the surface acidity of the material. The high hydrophobicity of GR compared to GO and, to a lower extent GR-SO₃H, could favor a hydrophobic environment susceptible of

accelerating or stabilizing reaction intermediates. However, this effect was also ruled out since the use of graphite and coronene, as simplistic mimics of GR, did not promote the acetalisation process (entries 10-11). The presence of metal impurities arising from the oxidation step, e.g., Mn, could be responsible of the activity of GR. However, the surface analysis of purified GR did not show impurities in a detectable extent (Fig. 2c) and, more importantly, the use of unpurified GR, having detectable Mn impurities, as determined by XPS analyses (Fig. S1, ESI), displayed a reduced activity, even after prolonged reaction times (entry 12). At this time, it is premature to definitively conclude on the specific role of GR but its unique electronic properties are likely responsible for this uncovered reactivity under acid-free conditions. The acetalisation of glycerol with benzaldehyde provided a mixture of (2phenyl[1,3]dioxolan-4-yl)methanol 3a and 2-phenyl[1,3]dioxan-5-ol **3b**, as previously mentioned in the literature.²⁸ Analysis by ¹H NMR showed the formation of four isomers corresponding to two pairs of diastereoisomers arising from a nearly equimolar cis/trans mixture of five and six-membered acetals. The chemical shift values (δ) of signals accounting for the acetal proton [-OCH(Ph)O-] of 3a-b are depicted in Table 3 along with the characteristic proton signals of the compounds prepared in this study. The formation of the fivemembered ring 3a was kinetically favored with GR in our reaction conditions, with a 3a/3b selectivity of 63/37 and a GR loading of 25 mg mmol⁻¹ of glycerol. Deutsch and Lieske observed a progressive evolution of five to six-membered acetals upon extended reaction times with Amberlyst-36 as catalyst, an outcome rationalized by an acid-catalyzed equilibrium between **3a** and **3b**.⁴⁸ The same behavior was also reported by Adam et al. using sulfonic acid immobilized onto silica.⁴⁹ This trend was not observed with GR, even after 14 hours of stirring; the absence of any acidic function in our system obviously precluding such an equilibrium (entry 4 vs. 8). By contrast, an equilibrium leading to an evolution of the selectivity was indeed observed with GR-SO₃H (entry 2 vs. 3), but in these cases, isomer 3b was kinetically favored, while 3a was the thermodynamic acetal. Actually, the survey of recent literature results on the acetalisation of glycerol with benzaldehyde did not provide any rational explanation and the 1,3-dioxolane/1,3-dioxane ratio likely depends on both the nature of the catalyst and torsional effects in acetal rings.

With these promising results in hand we further explored the behavior of GR for the acetalisation of glycerol with a collection of carbonyl compounds (Table 2).

Table 2	Acetalisation of glycerol with carbonyl compounds.
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НО	$0H \qquad 0$	GR, n 2 h, 100	eat ▶) °C ^a ∫' Oł	$ \begin{array}{c} R^{1} \\ O \\ \downarrow \\ W \\ R^{2} \\ \downarrow \\ O \\ \downarrow \\ H \end{array} + \begin{array}{c} R \\ P \\ P \\ \downarrow \\ H \end{array} $	¹ R ² V O OH
Entry	Carbonyl	Catalyst	Time	Selectivity	Yield
	compound		(h)	5-mem/6-	(%) ^b
				mem	
1	Benzaldehyde	GR	2	63/37	91
2	Benzaldehyde	GR-	2	33/67	49
		SO₃H			
3	Anisaldehyde	GR	2	63/37	99

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4	trans-	GR	2	66/34	89	trans-	-OC H (Ar)O-	5.59 (s), 5.45 (s) / 5.19
	Cinnamaldehyde					Cinnamaldehyde		(s), 5.07 (s)
5	Furfural	GR	2	68/32	85 [°]	Furfural	-OC H (Fur)O-	6.04 (s), 5.89 (s) / 5.61
6	Acetone	GR	2	>99/<1	76			(s), 5.50 (s)
7	Acetone	GR	2	>99/<1	85 ^d	Acetone	-OC(CH ₃) ₂ O-	1.45 (d) ^a , 1.38 (d) ^a / ND
8	Acetone	GR-	14	>99/<1	59 ^d	Acetophenone	-OC(C H ₃)(Ph)O-	1.72 (s), 1.69 (s) / ND
		SO₃H				Cyclopentanone	-OCH(R)C H 2-OH	$3.48 (dd)^{b}$, $3.56 (dd)^{c}$ /
9	Acetone		14		0 ^{<i>d</i>}			ND
10	Acetophenone	GR	2	>99/<1	25	Cyclohexanone	-OCH(R)C H 2-OH	$3.52 (dd)^d$, $3.59 (dd)^e$ /
11	Acetophenone	GR	2	>99/<1	72 ^d			ND
12	Cyclopentanone	GR	2	>99/<1	99	^a J = 0.6 Hz. ^b J = 4.8, 11.2 Hz. ^c J = 4.8, 11.6 Hz. ^d J = 4.8, 11.6 Hz. ^e J =		
13	Cyclohexanone	GR	2	>99/<1	99	4.8, 11.6 Hz		

^{*a*} Reaction conditions: glycerol **1** (1 mmol), carbonyl compound (10 mmol) and the catalyst (25 mg) were stirred at 100-120 °C for the indicated time. ^{*b*} ¹H NMR yield using 1,3,5-trimethylbenzene as internal standard. ^{*c*} 12.5 mg of GR was used. ^{*d*} Reaction carried out at 120 °C.

A similar selectivity, still in favor of the kinetically controlled fivemembered cyclic acetal, was observed with both aldehydes and ketones. Tuning the electronic properties of aldehydes did not significantly modify the reaction outcome (entries 1-5). We underline the remarkable reactivity of GR that allows a lower catalyst loading (12.5 mg mmol⁻¹ of glycerol) when furfural was used as acetalisation reagent (entry 5). This high selectivity favorably competes with those extracted from literature precedents.⁵⁰⁻⁵³ The synthesis of 2,2-dimethyl-1,3-dioxolan-5-ol, also known as solketal, from glycerol and acetone is a relevant process for the gasoline industry. Solketal has been used as a highly soluble fuel additive increasing the octane number by 2.5 units. Usually, the condensation of glycerol with acetone under acidic conditions gives a mixture of five- and six-membered acetals, with a high selectivity in favor of solketal (>90%). Although acetone was expected to be less reactive than aldehyde, GR exhibited a comparable activity, producing solketal as the only detectable compound in 76% yield at 100 °C and even 85% yield at 120 °C (entries 6-7). By contrast, GR-SO₃H displayed a much lower activity since solketal was selectively produced in only 59% after 14 hours of stirring (entry 8), while no product could be detected in the absence of catalyst (entry 9). A perfect selectivity in favor of the five-membered acetal was observed with other ketones (entries 6-13). Acetophenone proved to be less reactive in the reaction conditions, likely due to steric hindrance, though a good yield was obtained by increasing the temperature from 100 to 120 °C (entries 10 vs 11). By contrast, steric hindrance did not affect the reactivity of cyclic ketones that gave quantitatively and selectively the corresponding five-membered acetals at 100 °C (entries 12-13).

Table 3. Identification of characteristic chemical shifts by ¹H NMR (400 MHz).

1			
Reactant	Proton signal	Chemical shift (ppm)	
		5-mem / 6-mem	
Benzaldehyde	-OC H (Ph)O-	5.97 (s), 5.83 (s) / 5.55	
		(s), 5.43 (s)	
Anisaldehyde	-OC H (Ar)O-	5.90 (s), 5.77 (s) / 5.50	
		(s), 5.38 (s)	

3.3. Recycling studies

The reusability of the catalyst is a crucial feature when developing a sustainable process. The reuse of GR was explored for the acetalisation of glycerol with benzaldehyde on four consecutive runs (Fig. 3). After completion of each run, the reaction mixture was filtered on a nylon membrane, the catalyst was washed with water and acetone to remove adsorbed reagents and then dried under vacuum. Only a slight decrease was observed upon successive reuses, suggesting that GR was very stable in the reaction conditions. We also note that the selectivity in favor of the fivemembered acetal, with respect to the six-membered one, slightly increased from 65/35 for the first run to 80/20 for the fourth one. A close examination of the yields obtained for each isomer (dioxolane vs dioxane), revealed that this increased selectivity was attributed to the slight erosion of the yield for the six-membered acetals while the vield for the five-membered isomers remained constant over the successive reuses. This unexpected behavior is still under investigation in our laboratory. The yield significantly decreased after the fifth run. Neither the elemental composition, nor the aggregation state of GR were affected after the fifth reuse as supported by XPS and XRD analyses (Fig. S2 and S3, ESI). Therefore, the catalyst deactivation was attributed to the surface fouling by polyoxygenated organic residues, disrupting the contact of reagents with the GR surface. This was supported by TEM images showing GR sheets covered by a cloudy material (Fig. S4, ESI). To address this issue, GR was thoroughly washed with water and ethanol in an ultrasonic bath after the fifth run. Gratifyingly, the catalytic activity for the five-membered acetal was fully restored in the sixth reuse, confirming that the GR integrity was conserved. A similar study was conducted with acetone as substrate and confirmed the good recyclability of GR, since after the third run the yield for solketal reached 81% (vs. 85% for the first run).

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Fig. 3 Recycling studies.

4. Conclusion

In summary, we described in this contribution how serendipity led to the discovery of new properties of graphene for the successful acetalisation of glycerol with aldehydes and ketones in neutral conditions. Importantly, graphene features high catalytic activity and excellent recyclability properties for the production of high added value acetals. Preliminary mechanistic studies suggested that the high activity unveiled for graphene could not be ascribed to residual acids nor metallic cations and could rather be attributed to the peculiar electronic properties of the honeycomb-structured 2D material. We are currently exploring in depth the exact role of graphene in this process and we expect that this uncovered activity could also be applied to other, especially those involving the transformation of carbonyl compounds.

Acknowledgements

We gratefully acknowledge the University of Nantes, the "Centre National de la Recherche Scientifique" (CNRS), the "Région Pays de la Loire" in the framework of a "recrutement sur poste stratégique". F.-X.F. is a member of the "Institut Universitaire de France" (IUF). We acknowledge Christine Labrugère (PLACAMAT, University of Bordeaux), Julie Hémez (CEISAM, University of Nantes) and Nicolas Stephant (IMN, University of Nantes) for XPS, TEM and SEM analyses respectively. Prof. Denis Jacquemin (CEISAM, University of Nantes) is gratefully acknowledged for fruitful discussions and careful proofreading.

Notes and references

- 1 A. Demirbas, *Energy Policy*, 2007, **35**, 4661-4670.
- 2 K. Bozbas, Renew. Sustain. Energy Rev., 2008, **12**, 542-552.
- 3 P. N. R. Vennestrøm, C. M. Osmundsen, C. H. Christensen and E. Taarning, Angew. Chem. Int. Ed., 2011, 50, 10502-10509.
- 4 J. A. Melero, J. Iglesias and A. Garcia, *Energy Environ. Sci.*, 2012, **5**, 7393-7420.
- 5 R. A. Sheldon, *Green Chem.*, 2014, **16**, 950-963.

- M. J. Climent, A. Corma and S. Iborra, *Green Chem.*, 2014, **16**, 516-547.
- A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411-2502.
- M. Hara ChemSusChem, 2009, 2, 129-135.
- S. Yan, C. DiMaggio, S. Mohan, M. Kim, S. Salley and K. Y. S. Ng, *Top. Catal.*, 2010, **53**, 721-736.
- 10 C.-H. Zhou, X. Xia, C.-X. Lin, D.-S. Tong and J. Beltramini, *Chem. Soc. Rev.*, 2011, **40**, 5588-5617.
- J. M. Bernal, P. Lozano, E. Garcia-Verdugo, M. I. Burguete, G. Sanchez-Gomez, G. Lopez-Lopez, M. Pucheault, M. Vaultier and S. V. Luis, *Molecules*, 2012, 17, 8696-8719.
- 12 P. Gallezot, *Chem. Soc. Rev.*, 2012, **41**, 1538-1558.
 - M. Besson, P. Gallezot and C. Pinel, *Chem. Rev.*, 2013, **114**, 1827-1870.
 - A. F. Lee, J. A. Bennett, J. C. Manayil and K. Wilson, *Chem. Soc. Rev.*, 2014, **43**, 7887-7916.
 - D. Liu and E. Y. X. Chen, *Green Chem.*, 2014, **16**, 964-981.
 - F. Su and Y. Guo, Green Chem., 2014, 16, 2934-2957.
 - P. Cintas, S. Tagliapietra, E. Calcio Gaudino, G. Palmisano and G. Cravotto, *Green Chem.*, 2014, **16**, 1056-1065.
 - J. I. Garcia, H. Garcia-Marin and E. Pires, Green Chem., 2014, **16**, 1007-1033.
 - F. Chahdoura, I. Favier and M. Gomez, *Chem. Eur. J.*, 2014, **20**, 10884-10893.
 - Y. L. Gu, J. Barrault and F. Jerome, Adv. Synth. Catal., 2008, **350**, 2007-2012.
 - Y. L. Gu and F. Jerome, *Green Chem.*, 2010, **12**, 1127-1138.
- 22 M. Sutter, E. D. Silva, N. Duguet, Y. Raoul, E. Métay and M. Lemaire, *Chem. Rev.*, 2015, **115**, 8609-8651.
 - P. H. R. Silva, V. L. C. Gonçalves and C. J. A. Mota, Bioresour. Technol., 2010, **101**, 6225-6229.
- 24 M. J. Climent, A. Corma and A. Velty, *Appl. Catal. A: Gen.*, 2004, **263**, 155-161.
- A. Piasecki, A. Sokolowski, B. Burczyk and U. Kotlewska, J. Am. Oil Chem. Soc., 1997, 74, 33-37.
 - P. Sari, M. Razzak and I. G. Tucker, *Pharm. Dev. Technol.*, 2004, **9**, 97-106.
 - J. A. Dipietro, K. S. Todd and V. Reuter, *Am. J. Vet. Res.*, 1986, **47**, 874-875.
- 28 A. J. Showler and P. A. Darley, *Chem. Rev.*, 1967, **67**, 427-440.
- F. Jérôme, Y. Pouilloux and J. Barrault, *ChemSusChem*, 2008, 1, 586-613.
 - V. Georgakilas, A. B. Bourlinos, R. Zboril, T. A. Steriotis,
 P. Dallas, A. K. Stubos and C. Trapalis, *Chem. Commun.*,
 2010, 46, 1766-1768.
 - Z. Sun, S.-i. Kohama, Z. Zhang, J. Lomeda and J. Tour, Nano Res., 2010, **3**, 117-125.
 - J. M. Englert, C. Dotzer, G. Yang, M. Schmid, C. Papp, J. M. Gottfried, H.-P. Steinrück, E. Spiecker, F. Hauke and A. Hirsch, Nat. Chem., 2011, **3**, 279-286.

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DOI: 10.1039/C5GC02316E

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- V. Georgakilas, M. Otyepka, A. B. Bourlinos, V. Chandra, N. Kim, K. C. Kemp, P. Hobza, R. Zboril and K. S. Kim, *Chem. Rev.*, 2012, **112**, 6156-6214.
- F. M. Koehler and W. J. Stark, Acc. Chem. Res., 2012, 46, 2297-2306.
- S. P. Economopoulos and N. Tagmatarchis, *Chem. Eur. J.*, 2013, **19**, 12930-12936.
- 36 L. Rodriguez-Perez, M. a. A. Herranz and N. Martin, Chem. Commun., 2013, 49, 3721-3735.
- 37 C. Su and K. P. Loh, Acc. Chem. Res., 2012, 46, 2275-2285.
- 38 D. R. Dreyer, A. D. Todd and C. W. Bielawski, Chem. Soc. Rev., 2014, 43, 5288-5301.
- 39 S. M. Islam, A. S. Roy, R. C. Dey and S. Paul, J. Mol. Catal. A: Chem., 2014, **394**, 66-73.
- 40 S. Navalon, A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *Chem. Rev.*, 2014, **114**, 6179-6212.
- X. Fan, G. Zhang and F. Zhang, Chem. Soc. Rev., 2015, 44, 3023-3035.
- 42 S. Zhu, J. Wang and W. Fan, *Catal. Sci. Technol.*, 2015, 5, 3845-3858.
- 43 C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam and A. Govindaraj, *Angew. Chem. Int. Ed.*, 2009, **48**, 7752-7777.
- 44 M. J. Allen, V. C. Tung and R. B. Kaner, *Chem. Rev.*, 2010, **110**, 132-145.
- Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts and
 R. S. Ruoff, *Adv. Mater.*, 2010, **22**, 3906-3924.
- 46 V. Georgakilas, J. A. Perman, J. Tucek and R. Zboril, Chem. Rev., 2015, **115**, 4744-4822.
- 47 N. Oger, Y. F. Lin, C. Labrugère, E. Le Grognec, F. Rataboul and F.-X. Felpin, *Carbon*, 2016, **96**, 342-350.
- J. Deutsch, A. Martin and H. Lieske, J. Catal., 2007, 245, 428-435.
- 49 F. Adam, M. S. Batagarawa, K. M. Hello and S. S. Al-Juaid, Chem. Pap., 2012, 66, 1048-1058.
- 50 B. Mallesham, P. Sudarsanam, G. Raju and B. M. Reddy, Green Chem., 2013, **15**, 478-489.
- 51 C. Gonzalez-Arellano, R. A. D. Arancon and R. Luque, Green Chem., 2014, **16**, 4985-4993.
- 52 C. Gonzalez-Arellano, S. De and R. Luque, *Catal. Sci. Technol.*, 2014, **4**, 4242-4249.
- B. Mallesham, P. Sudarsanam and B. M. Reddy, *Catal. Sci. Technol.*, 2014, 4, 803-813.

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