Basified Graphene Oxide and PPO Composite Aerogel with Basified Graphene Oxide for Henry Reaction in Solvent-Free Conditions: A Green Approach

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ABSTRACT: Novel basified graphene oxide and high-porosity monolithic composite aerogels of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) containing basified graphene oxide (b-eGO) have been prepared as recoverable and reusable catalysts for the Henry reaction in solvent-free conditions at room temperature. The results showed that, although b-eGO was able to promote the reaction, it suffered from reduced stability. On the other hand, PPO/b-eGO aerogels were able to efficiently promote the Henry reaction in solvent-free conditions. The product could be obtained pure without a purification step, and the catalyst was stable for over 15 months and could be easily recycled without losing catalytic efficiency. The stereochemical outcome was further investigated in the presence of PPO/b-eGO. Despite its negligible influence on diastereoselectivity, better efficiency and a sensible reduction of reaction time were observed.

1. INTRODUCTION

The Henry reaction constitutes as one of the fundamental synthetic tools for generating C−C bond for the preparation of poly-functionalized molecules.[1−5] The nitroalkanols obtained can be used as valuable starting materials for chiral 1,2-amino alcohols and β-hydroxyl carboxylic acids due the versatile chemistry of the nitro group.[2] Moreover, optically active β-hydroxynitroalkanes are useful intermediates in the synthesis of several pharmacologically important compounds such as ephedrine, propanolol, and sphingosine.

Many procedures, acid- and base-catalyzed, with the ability to promote the reaction in good yield and enantioselectivity have been reported in the literature.[6,7] Metal and organic catalysts have been used in the homogeneous phase to assure a high level of efficiency and enantioselectivity[8−13] as well, but the ability to perform the reaction by using a heterogeneous catalyst is one of the goals to be achieved to make sustainable chemistry.

Furthermore, the possibility of eliminating the solvent and easily recovering the catalyst can ensure compliance with the basic criteria for green chemistry.

Recently, the use of nanostructure materials has been applied in catalysis research areas for elevating the efficiency of the catalytic transformations[14−17] and has received much attention due to their low cost, large surface area and porosity, chemical and thermal stability, mechanical strength, and simple synthesis.[18−21] Especially regarding the Henry reaction, mesoporous silica materials have been easily functionalized with the amine group to be utilized as retrievable solid base catalysts for heterogeneous Henry reactions.[22]

Moreover, the approach to amine functionalization has also been reported with graphite oxide providing a tri-amine functionalized graphene oxide able to catalyze, even in a nitrogen atmosphere and with high catalyst loading, the Henry reaction in solvent-free conditions.[23]

If the functionalization by amines of mesoporous silica materials or graphite oxide providing base catalysts can promote the Henry reaction, an alternative approach by performing a simple basification of the "support" could be desirable.

The well-known carbon materials are not "innocent" supports, as demonstrated by many recent publications within the carbocatalysis field. As a matter of fact, recently, they have emerged as cheap and metal-free catalysts and have attracted much attention regarding the use of graphite, graphite oxide (GO), and graphene oxide (eGO) in the oxidation reaction,[24−28] Friedel−Crafts reaction,[29] aza-Michael addition,[30] imination,[31] polymerization,[32] epoxy-ring opening reactions,[33,34] Mukaiyama−Michael reaction,[35,36] and cross-linking reaction.[37]

Moreover, in many reactions, the ability of carbon materials to be used in solvent-free conditions makes them very
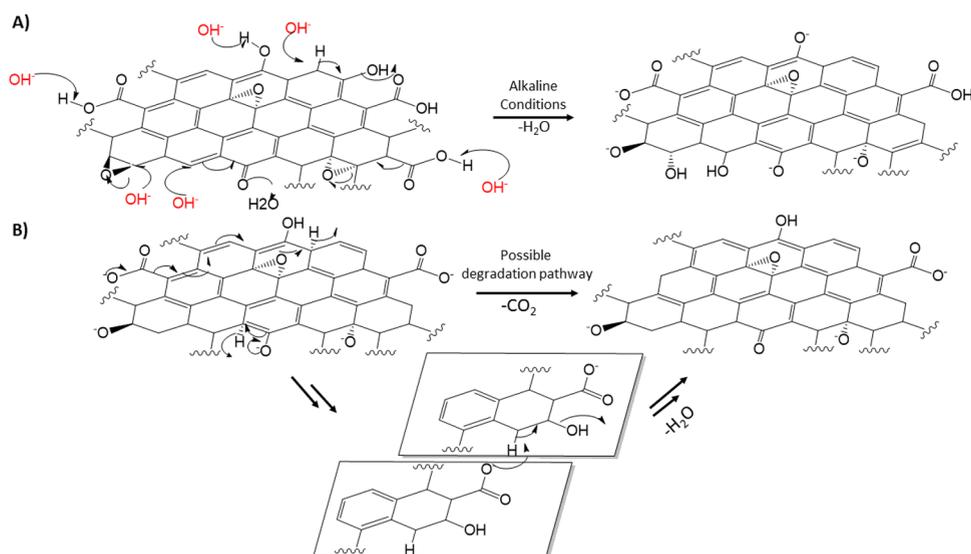
Figure 1. Schematic representation of NaOH treatment of e-GO to provide b-eGO (A) and possible degradation pathways (decarboxylation and dehydration) of b-eGO under alkaline conditions (B).

promising for further elaborating eco-sustainable procedures.[29,34−37]

Because of the presence of acidic groups, it is not difficult to imagine that an alkaline treatment of GO and eGO could give a possible catalyst for a reaction promoted by basic conditions (Figure 1A).

Specifically, the ability to provide many basic sites to promote the reaction could significantly reduce the amount of catalyst used and increase the productivity or turnover number (TON) of this reaction, i.e., molecules of nitroalkyl produced per active site. Furthermore, being heterogeneous can positively affect the reaction procedure.

Herein, we report the ability of basified graphene oxide (b-eGO) to efficiently promote the Henry reaction at room temperature, in solvent- and metal-free conditions with different aldehydes.

Although the reaction proceeds with good efficiency, the natural instability of the b-eGO due to the basification of the acidic functionalities, i.e., decarboxylation, dehydration, etc., (Figure 1B) driven by the need to restore the classical aromaticity of the plane, makes it unsuitable for a sustainable approach. This aspect does not assure the catalyst recyclability, making b-eGO a promoter rather than a catalyst.

To overcome this problem, a different approach could be used. Important results have already been obtained through the immobilization of organocatalysts on polymeric supports, providing efficient catalyst for aza-Henry reactions in solvent-free conditions.[38] The catalytic activity of these materials is dependent on a lot of parameters, including the accessibility of the reactants to the active site, whereas the recyclability and durability of the catalyst are dependent on the robustness of the bond linking the catalyst to the polymer, which can represent a possible limit.

Recently, we reported that monolithic aerogels based on nanoporous crystalline poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) polymers and reduced graphene oxide (r-GO) hybrid nanocomposites were prepared by making use of the advantages of nanoporous crystallinity of the polymers as well as the GO catalytic activity.[39] The composite formation is not due to bond linking, but to a good dispersibility of carbon materials in the polymer matrix.

Preliminary tests showed that PPO/r-GO aerogels were capable of absorbing benzyl alcohol from the diluted aqueous solutions and oxidizing a fraction of the sorbed benzyl alcohol molecules. Therefore, to possibly prevent b-eGO degradation and to make the catalyst recovery easy, a different approach was studied by preparing nanoporous crystalline PPO composite aerogels with basified graphene oxide.

Herein, we show that the new PPO/b-eGO aerogel composite can ensure a very simple procedure with an easy-to-handle catalyst, good efficiency, and simple product recovery without any further purification. The catalyst stability is surprisingly preserved, allowing it to be recycled and reused without losing efficiency.

2. RESULTS AND DISCUSSION

2.1. b-eGO and PPO/b-eGO Characterization. The X-ray diffraction patterns of the starting GO obtained by Hummers' method,[40] graphene oxide after milling (eGO), and basified graphene oxide (b-eGO) are reported in Figure 2.

The basification treatment has been applied to the eGO sample exhibiting an O/C molar ratio of 0.71, as obtained after milling of GO.

The X-ray diffraction pattern of oxidized graphite (GO) shows interlayer distance $d_{001} = 0.84$ nm, higher than the interlayer distance of the starting graphite (0.34 nm) and a well-defined 100 peak with $d_{100} = 0.21$ corresponding to the in-plane periodicities.

After oxidation, GO was milled, providing eGO, which shows the disappearance of the 001 reflection replaced by a very broad intense halo, centered at a d of 0.37 nm with a correlation length of ∼1 nm, indicating the presence of a large fraction of essentially exfoliated GO.

After the basification treatment, performed by using 0.05 M NaOH solution, we observed in the X-ray diffraction pattern the maintenance of the in-layer graphitic order (100 reflection plans), a broad reflection centered at d of 0.36 nm and the complete disappearance of the 001 peak, which clearly indicated the formation of fully exfoliated b-eGO.
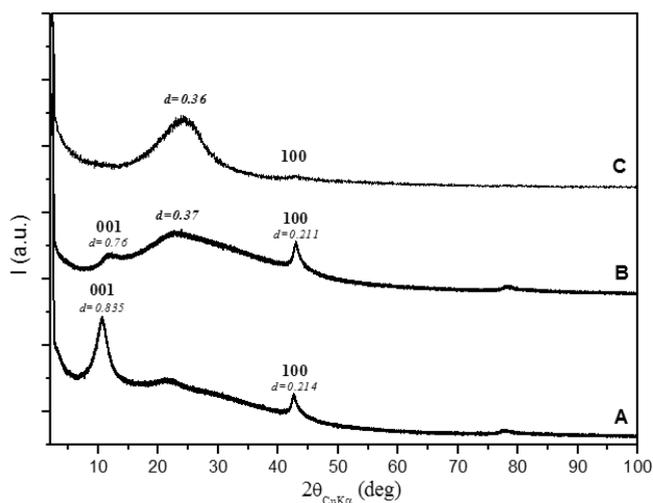
Figure 2. X-ray diffraction patterns of GO obtained by Hummers' method (A), the resultant graphene oxide obtained after milling (B), and basified graphene oxide as for alkaline treatment (C).

Furthermore, IR analysis of the starting GO sample, after milling (e-GO) and basification (b-eGO), is reported (Figure 3). Significant changes of wavenumber are clearly shown going from eGO to b-eGO mainly regarding the typical carboxylic group band located at 1730 cm^{-1} that is shifted to 1680 cm^{-1} for the alkaline treatment, resulting in the formation of carboxylate groups.[41]

Moreover, after basification, more defined and narrower bands appear at 1345 and 1057 cm^{-1} (C−O stretching vibrations) as a consequence of epoxy-ring opening and sodium phenolate formation.[42]

The homogeneously dispersed monolithic aerogels of polymer/b-eGO nanocomposite, were prepared following the method already reported in our previous paper.[39]

In the first step, the freshly prepared b-eGO was dispersed in methyl benzoate solvent and sonicated for 30 min at room temperature. Then, polymer was added to this stable dispersion and after complete dissolution of the polymer and obtaining a homogeneous solution by heating at 120 °C, the solution was cooled down to room temperature where the gelation occurred. Subsequently, the gel solvent was extracted with supercritical carbon dioxide (scCO$_2$), which led to the

formation of monolithic aerogels with uniformly dispersed polymer/b-eGO nanocomposites. The final PPO/b-eGO ratio was 80:20 with a total porosity about 90%.

The X-ray diffraction patterns also showed that, after the guest (solvent) extraction procedure, nanoporous crystalline polymer phases were obtained for both PPO and composite aerogel. Curve B (Figure 4) of the PPO$_{0.8}$/b-eGO$_{0.2}$ aerogel
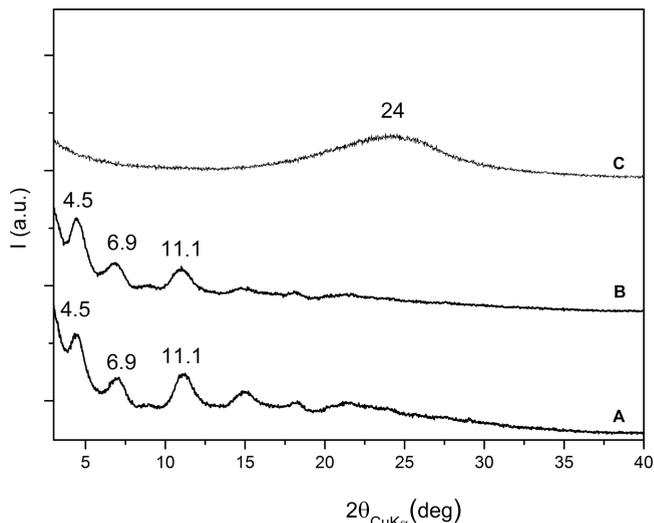

Figure 4. X-ray diffraction patterns of (A) PPO aerogel; (B) hybrid monolithic polymer aerogels of PPO$_{0.8}$/b-eGO$_{0.2}$ nanocomposites containing 20 wt % of b-eGO; (C) b-eGO.

diffraction pattern appeared with diffraction reflections at 2θ = 4.5, 6.9, and 11.1° corresponding to the α PPO nanoporous crystalline structure modification.[43] The 002 reflection corresponding to b-eGO at 2θ = 24.0° was not detected in the nanocomposites, clearly indicating that most of the b-eGO was constituted by structural layers exhibiting negligible order in the direction perpendicular to the graphitic structure.

The surface areas of PPO, the composite aerogels, and b-eGO were determined by BET measurement. While the surface area for pure PPO is 700 m^{2}g^{-1} and b-eGO used for the preparation of the composite aerogels exhibited a value of 4 m^{2}g^{-1}, surface area of PPO$_{0.8}$/b-eGO$_{0.2}$ composite aerogels reached 603 m^{2}g^{-1} even in the presence of 20 wt % of b-eGO.
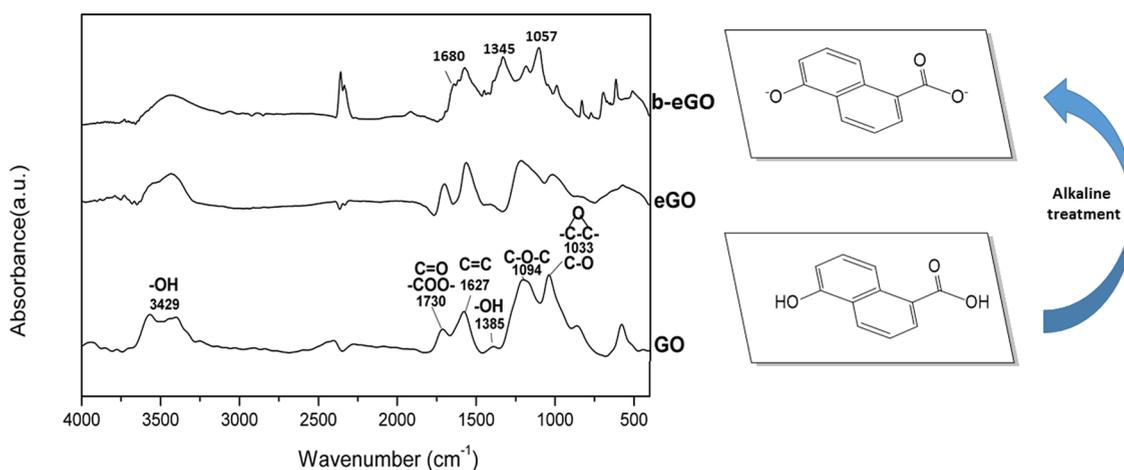

Figure 3. FTIR spectra of the GO sample, after milling (eGO), and after alkaline treatment (b-eGO).

This result is very important because catalyst supports must provide a considerably large surface area.

2.2. Henry Reaction with b-eGO Powder and PPO/b-eGO. The b-eGO powder characterized in Figures 2 and 3 has been used as possible catalysts for the Henry reaction of nitromethane and different aromatic aldehydes at room temperature and in solvent-free conditions (Scheme 1). In

Scheme 1. Henry Reaction of Nitromethane with Different Aromatic Aldehydes
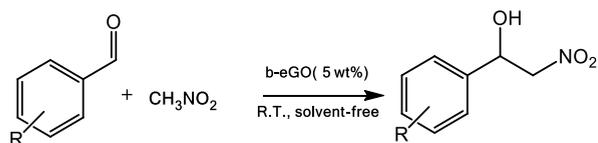
the absence of a catalyst, under solvent-free conditions, the reaction provides traces of the product, while by adding 5 wt % b-eGO loading, high conversion was obtained already after 5 h

with p-nitrobenzaldehyde (entry 1, Table 1). As an attempt to reduce the catalyst loading, the reaction was also performed with 2 wt % of b-eGO, but remarkable reduction in efficiency and increased reaction time were observed.

Full conversion was obtained also by performing the reaction with p-cyanobenzaldehyde, even in prolonged reaction times. The changing of electron-withdrawing properties and the position of the substituents on the benzene ring affects the reaction time and the conversion as well.

According to the electron-withdrawing scale of aromatic substituents, going from the stronger nitro group to medium strong trifluoromethyl until medium cyano and weak chlorine group (entries 1, 2, 4, and 6, Table 1), longer reaction times are needed to achieve high conversions. Mainly regarding the influence of chlorine group, it was possible to obtain only 35% of conversion after 21 days.
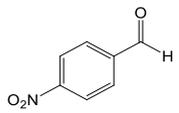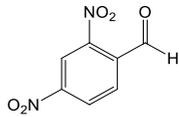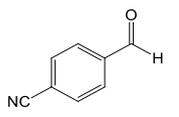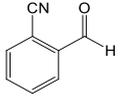
Furthermore, the ortho position of the substituent negatively affects the reaction time, especially for the steric hindrance,

Table 1. Henry Reaction Performed with Different Activated Aryl Aldehydes in the Presence of 5 wt % of b-eGO

entry	aldehyde	days	conversion (%)[a]
1		0.2	>99%
2		1	>99%
3		1	>99%
4		2	80%
5		7	91%
6		14	Traces
7		7	35%

[a]The conversion was detected by ^{1}H-NMR analysis for all the reaction reported.

Table 2. Henry Reaction Performed with Different Activated Aryl Aldehydes in the Presence of $PPO_{0.8}$/b-$eGO_{0.2}$ Composite Aerogels, with 5 wt % of Catalyst
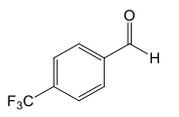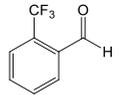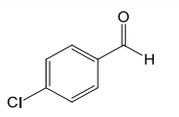
entry	aldehyde	days	conversion (%)[a]
1	(4-nitrobenzaldehyde)	3	>99%
2	(2,4-dinitrobenzaldehyde)	3	>99%
3	(4-cyanobenzaldehyde)	3	>99%
4	(2-cyanobenzaldehyde)	3	80%
5	(4-trifluoromethylbenzaldehyde)	10	91%
6	(2-trifluoromethylbenzaldehyde)	10	Traces
7	(4-chlorobenzaldehyde)	10	35%

[a]The conversion was detected by ^{1}H-NMR analysis for all the reaction reported.

providing for not highly activated benzene just traces of product even after 14 days (entry 5, Table 1).

For all the reactions, b-eGO was easily recovered by aqueous solvent extraction and the product by ethyl acetate as ecofriendly solvent.

Finally, we investigated the recyclability of the recovered b-eGO, but already after the second run, the efficiency was deeply decreased.

This is not surprising because the b-eGO presents an extremely reduced temporal stability due to its natural tendency to degrade (i.e., decarboxylation, dehydration, etc.) (Figure 1B) and to restore the classical aromaticity of the plane. According to the elemental analysis on the fresh and 1—week-old sample, a sensible reduction of the oxygen content was detected going from 0.71 to 0.61 O/C for fresh and 1-week-old sample, respectively.

This aspect has been further verified during the experiments because b-eGO powder had to be prepared several times, as it

showed extremely low catalytic activity within days of initial use.

Since the possibility of supporting carbon nanomaterial in polymer matrices is already known, as reported in our previous paper,[39] we prepared high-porosity monolithic composite aerogels of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) containing basified graphene oxide (PPO/b-eGO).

The final PPO/b-eGO ratio 80:20 was chosen to have both the right amount of catalyst useful for providing efficient reactions and using reasonable sized nanocomposite slice with good mechanical properties.

Therefore, the reactions were performed by using $PPO_{0.8}$/b-$eGO_{0.2}$ composite aerogels in the right amount to ensure the presence of 5 wt % of b-eGO in the reaction system (Table 2).

The use of $PPO_{0.8}$/b-$eGO_{0.2}$ composite aerogels provides the same efficiency as already shown for b-eGO, although in a longer reaction time, possibly due to the lower diffusion rate of the reagents into the supported catalyst.

The product recovery procedure is instead easier due to both the possibility to wash the aerogel slice with ethanol and taking the product without any further purification for 99% conversion, and the simple recovery of the supported catalyst after reaction.

Finally, the reusability of supported b-eGO was investigated using the addition of nitromethane to p-nitrobenzaldehyde as the model reaction.

The $PPO_{0.8}$/b-$eGO_{0.2}$ composite aerogels, recovered after washing with ethanol and dried at 60 °C overnight, was used without any further treatment. The reaction conditions, room temperature, and duration of 3 days were kept the same for all the cycles. Surprisingly, as shown in Figure 5, the yield of the reaction remained unchanged after 4 runs.
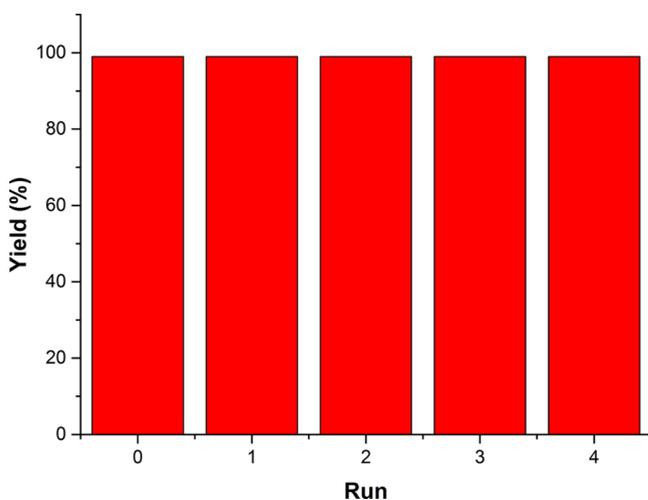

Figure 5. Yields from recycling experiments.

The same results were obtained by $scCO_2$ treatment to empty the cavities of the composite aerogel.

Despite of the intrinsic instability of b-eGO, the composite aerogel preserves the catalytic activity and stabilizes the catalyst, providing a sustainable procedure.

The origin of this stabilization effect was investigated by performing WAXD measurements on the freshly prepared nanocomposites and aged $PPO_{0.8}$/$bGO_{0.2}$ after 15 months. The WAXD pattern of both samples is absolutely superimposable (Figure 4B), clearly indicating that b-eGO does not aggregate even after 15 months.

Further tests were carried out to verify the stability of the catalyst, performing the reaction in the presence of aging $PPO_{0.8}$/$bGO_{0.2}$. Specifically, after 15 months, the reaction was repeated in the same reaction conditions providing 99% conversion as for the reaction performed with freshly prepared composite (entry 1, Table 1).

So the reason for this stabilization effect could be possibly due to the good dispersion of the b-eGO powder in the polymer matrix, which reduces the possibility of interaction between the basic active sites present on its surface, thus preventing degradation reactions such as decarboxylation or dehydration (see Figure 1B).

In the attempt to improve the efficiency and to evaluate the possible stereochemical induction using graphitic materials, a further investigation was performed using bromonitromethane (Scheme 2).

Scheme 2. Henry Reaction of Bromonitromethane with Different Aromatic Aldehydes
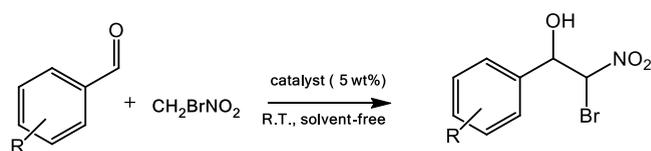
The influence on the diastereoselective ratio could be possible as previously reported for the Mukaiyama−Michael reaction,[35] where an unprecedent inversion of diastereoselectivity was detected due to π-stacking interactions between the electrophile and the graphitic π system.

As for the precedent reactions, for the sake of comparison, both b-eGO as powder and PPO/b-eGO were used for all the experiments at room temperature and in solvent-free conditions to verify the possible influence of the support on the stereochemical pathway of the reaction.

As reported in Table 3, high efficiency and reduced reaction times are allowed to be reached in the presence of the more reactive bromonitromethane even if in all the cases both catalysts showed poor diastereoselective control. Intriguing results are obtained for oCN-benzaldehyde and oCF_3-benzaldehyde (entries 4 and 6, Table 3). Irrespective of the steric hindrance of substituents in the ortho position, the reactions performed in the presence of PPO/b-eGO composite aerogels provided the product in 99% conversion, in 3 days, while in the presence of the b-eGO, the same reactions do not proceed at all. It has to be noted that, with most of the substrates, the reaction times are comparable irrespective of the powder or composite aerogels used, while in entries 1 and 5, they are even higher for b-eGO powder. Despite the higher bromonitromethane nucleophilicity, this behavior may result from the aggregation of e-GO powder, reducing the number of basic sites available to catalyze the reaction and promoting the known degradation/reduction mechanism associated with this material. No substantially differences are, instead, present for the stereochemical outcome by using b-eGO as powder or as a composite.

3. CONCLUSIONS

The ability of b-eGO to efficiently promote the Henry reaction at room temperature, in solvent- and metal-free conditions with different aldehydes, has been reported.
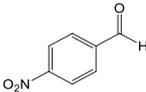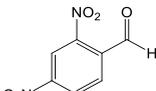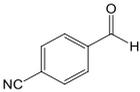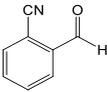
The reaction proceeded with high conversion, with most of the substrates showing a dependence on the reaction time from steric and inductive properties of the substituents. Due to its remarkable instability, b-eGO does not assure the catalyst recyclability being a promoter rather than a catalyst.

To overcome this problem, a new approach was used by preparing nanoporous crystalline PPO composite aerogels with basified graphene oxide.

Herein, we have shown that the new PPO/b-eGO composite aerogel is able to ensure high efficiency with a very simple procedure and easy product recovery without any purification. The catalyst stability is preserved for a long time, without losing efficiency even after 15 months.

In an attempt to evaluate the possible stereochemical induction by using graphitic materials, to improve the efficiency and to reduce the reaction times, a further investigation was performed using bromonitromethane. Although negligible influence on the stereochemical outcome

Table 3. Henry Reaction Performed with Bromonitromethane with Different Activated Aryl Aldehydes in the Presence of b-eGO and $PPO_{0.8}$/b-$eGO_{0.2}$ Composite Aerogels

entry	catalyst	aldehyde	days	conversion (%)[a]	D.r.(syn/anti)[b]
1	b-eGO	4-nitrobenzaldehyde (O_2N–C6H4–CHO)	3	>99	46/54
	PPO/b-eGO		0.3	>99	44/56
3	b-eGO	2,4-dinitrobenzaldehyde	0.3	>99	63/37
	PPO/b-eGO		0.3	>99	63/37
2	b-eGO	4-cyanobenzaldehyde (NC–C6H4–CHO)	2	>99	41/59
	PPO/b-eGO		3	>99	43/57
4	b-eGO	2-cyanobenzaldehyde	3	Traces	
	PPO/b-eGO		3	82	63/37
5	b-eGO	4-(trifluoromethyl)benzaldehyde (F_3C–C6H4–CHO)	5	79	43/57
	PPO/b-eGO		3	99	40/60
6	b-eGO	2-(trifluoromethyl)benzaldehyde	3	Traces	
	PPO/b-eGO		3	99	38/62
7	b-eGO	4-chlorobenzaldehyde (Cl–C6H4–CHO)	6	89	39/61
	PPO/b-eGO		8	83	38/62
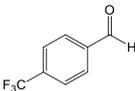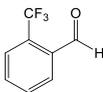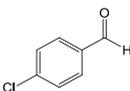
[a]The conversion was detected by ^{1}H NMR analysis for all the reactions reported. [b]The diastereoisomeric ratio was evaluated using the ^{1}H NMR spectra.

was detected, a sensible reduction of reaction times and better efficiency was provided due to the higher reactivity of the nucleophile.

For all the reactions reported, the use of basified graphene oxide as PPO/b-eGO composite aerogels, allows to prevent b-eGO degradation and to recycle the catalyst many times without losing efficiency. The composite is easy-to-handle and ecofriendly, assuring to provide and recover the product in very simple way, without any further purification.

4. MATERIALS AND METHODS

4.1. Materials. The high-molecular-weight PPO (Ultra High P6130 grade; M_w = 350 kg mol^{-1}) used in this study was kindly supplied by Sabic (Bergen op Zoom, The Netherlands). Graphite, with an 8427 trademark, was purchased from Asbury Graphite Mills Inc. (Asbury, OH, USA). Solvents and other reagents used in this work were purchased from Sigma Aldrich (St. Louis, MO, USA) and used as received.

All the chemicals used were purchased from Sigma Aldrich and used without any further purification. TLC was performed on silica gel 60 F254 0.25 mm on glass plates (Merck), and nonflash chromatography was performed on silica gel (0.063–0.200 mm, Merck). All ^{1}H NMR and ^{13}C NMR spectra were recorded with a DRX 400 and 300 MHz Bruker instrument, by using $CDCl_3$ (δ = 7.26 ppm in ^{1}H NMR spectra and δ = 77.0 ppm in ^{13}C NMR spectra) as the solvent (400.135 and 300.135 MHz for ^{1}H and 100.03 and 75 MHz for ^{13}C NMR). Mass spectrometry analysis was carried out using an electrospray spectrometer Waters 4 micro quadrupole. The elemental analyses were performed with FLASH EA 1112 Thermo equipment. Melting points were determined with the Electrothermal 9100 apparatus.

Surface area of monolithic polymer aerogels were obtained by N_2 adsorption measurements carried out at 77 K on a Nova Quantachrome 4200e sorption analyzer (Odelzhausen, Germany). The specific surface area of the aerogels was calculated using the Brunauer–Emmet–Teller method.

4.2. Graphene Oxide and Basified Graphene Oxide Synthesis. Hummers' method was adapted to the synthesis of GO [38]. Briefly, 120 mL of H_2SO_4 and 2.5 g of $NaNO_3$ were introduced into a 2000 mL three-neck round-bottomed flask containing 5 g of pure graphite powder. After that, 15 g of $KMnO_4$ was also added slowly with magnetic stirring; during this process, the oil bath temperature was maintained below 10

°C. Subsequently, the reaction temperature was increased to 35 °C and continued overnight. At the end of the reaction, 700 mL of deionized water and 5 mL of H_2O_2 (30 wt %) was added to the reaction mixture and removed from the oil bath. Additionally, 7 L of deionized water was added and then centrifuged at 10,000 rpm for 15 min with a Hermle Z 323 K centrifuge. Then, the isolated GO powders were repeatedly washed with a 5 wt % HCl aqueous solution and later with deionized water. Finally, the GO powders were collected and dried at 60 °C for 12 h.

Exfoliation of graphite oxide was performed by ball-milling, introducing GO powders in 125 mL ceramic jars (inner diameter of 75 mm) together with stainless-steel balls (10 mm in diameter) and dry-milled in a planetary ball mill S3 (Retsch GmbH 5657 Haan) for 2 h with a milling speed of 500 rpm and a ball-to-powder mass ratio of 10 to 1.

The cation-exchange-capacity of the obtained GO was determined as CEC_{GO} = 7.3 mmol/g, by the procedure reported by Matsuo et al.[44]

The basified GO (b-eGO) was prepared starting from eGO powders (360 mg) dispersed in 0.05 M NaOH solution (196 mL), and the reaction mixture was stirred at room temperature for 1 h. The slurry was centrifugated at 10,000 rpm for 15 min, and the precipitate was washed with deionized water and dried at 60 °C for 12 h in an oven.

4.3. Henry Reaction with b-eGO Powder. The reaction was conducted in a vial. p-Nitrobenzaldehyde (0.26 mmol) and nitromethane (1.8 mmol) were added to b-eGO powder (5 wt %) at room temperature. The reaction mixture was stirred at the same temperature for the time indicated. The reaction mixture was extracted with AcOEt, and the combined organic phase was dried (MgSO$_4$) and concentrated. The conversion was evaluated by ^{1}H NMR. The b-eGO powder was recovered by aqueous solution.

4.4. Henry Reaction with PPO/Be-GO Aerogel. The reaction was conducted in a vial. p-Nitrobenzaldehyde (0.26 mmol) and nitromethane (1.8 mmol) were added to PPO$_{0.8}$/b-eGO$_{0.2}$ containing 5 wt % of b-eGO at room temperature. The reaction mixture was maintained without stirring at the same temperature for the time indicated. In the presence of 99% conversion, the pure product was obtained by washing with ethanol without any other purification.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02335.

> Chemical details, synthesis details (GO and b-eGO), reaction details, FTIR (PPO, PPO/b-eGO), Characterization techniques, SEM images and ^{1}H-NMR and ^{13}C-NMR spectra (PDF)

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Notes
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