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Graphene oxide as an acid catalyst for the room temperature ring opening of epoxides†

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The minute amount of hydrogen sulfate groups introduced into the graphene oxide (GO) obtained by Hummers oxidation of graphite renders this material as a highly efficient, recyclable acid catalyst for the ring opening of epoxides with methanol and other primary alcohols as nucleophile and solvent.

Graphene and related materials have attracted much interest in nanoelectronics due to the fast charge mobility, high mechanical resistance and the fact that they represent the thickness limit for an electrically conductive material.[1,2] Triggered by these remarkable properties,[3] the interest in graphene-like materials has expanded to other areas in chemistry including adsorption and photocatalysis,[4–6] heterogeneous catalysis[7] and biosensors.[8] The high solubility, high surface area[9] and the fact that there are no barriers to mass transfer for substrates reaching the graphene surface make these materials also very suitable in catalysis as a new form of carbon.[10,11]

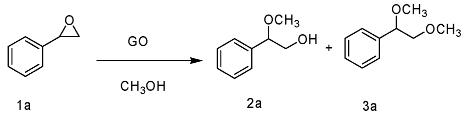
One of the most convenient ways to obtain graphene in large quantities is by graphite oxidation followed by exfoliation of the resulting graphene oxide to obtain highly persistent aqueous suspensions of graphene oxide (GO). The most widely applied oxidation conditions, the Hummers method[12] is based on the exhaustive oxidation of graphite using strong acid conditions by permanganate and hydrogen peroxide. In the present manuscript, we report that the GO obtained by the conventional Hummers method is a highly efficient, recyclable acid catalyst for the ring opening of epoxides with methanol. The available data suggest that the minor sulfate groups present in the GO are sufficient to act as recoverable and recyclable Brönsted acid sites.

Recently, GOs have been used as catalysts[13] in the oxidation of sulfides and thiols,[14] oxidation of benzylic positions[15] and benzyl alcohol.[16] In addition, reduced graphene oxide has also been used as catalyst for the room temperature reduction of nitrobenzene.[17] In a recent precedent, sulfated graphene obtained by hydrothermal sulfation of reduced graphene oxide with fuming sulfuric acid at 180 °C was tested as catalyst for the esterification of acetic acid, the Pechmann condensation and hydration of propylene oxide.[18] The difference between the material used in this prior work and the present one is that we are using here directly the GO samples obtained by the conventional Hummers oxidation without any subsequent treatment. Our GO is, therefore, more conveniently prepared and does not require additional and hazardous treatments.

The sample of GO used in the present study was obtained by Hummers oxidation of graphite followed by exfoliation in aqueous solution. The resulting GO was recovered by collecting the non-sedimented supernatant solution after centrifugation at 15 000 rpm and freeze drying.

The activity of GO as an acid catalyst was tested for the ring opening of epoxides using **1a** as a substrate in methanol as solvent and nucleophile at room temperature as a model reaction. The observed results are given in Table 1. In the absence of the catalyst, unreacted **1a** was recovered. When the

Table 1 Ring opening of styrene oxide with methanol catalyzed by GO and other catalysts[a]



Run	Catalyst	Time/min	Conversion[b] (%)	Selectivity[b] (%) 2a	3a
1	GO	10	91	99	1
2	GO	20	96	96	4
3	GO	60	99	93	7
4	GO	60	2[c]	100	—
5	GO	60	99[d]	97	3
6	GO	60	69[e]	91	9
7	GO	240	97[e]	90	10
8	GO	360	98[e]	90	10
9	Norit A	60	5	99	—
10	H_2SO_4	5	99	99	—
11	p-CH_3–C_6H_4–SO_3H	5	99	99	—
12	CH_3COOH	60	—	—	—

[a] Reaction conditions: **1a** (1 mL), methanol (10 mL), catalyst (5 mg), room temperature. [b] Determined by GC. [c] With 0.1 mL of pyridine. [d] After third reuse. [e] Reaction conditions: **1a** (3 mL), methanol (15 mL), catalyst (2 mg), room temperature.

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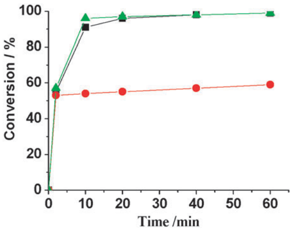


Fig. 1 Time-conversion plot for the ring opening of **1a** with methanol (squares) and filtration test (circles). Triangles represent the time-conversion plot for a different sample of GO obtained in an independent batch.

reaction of **1a** and methanol was carried out at room temperature in the presence of GO, almost >99% conversion with 93% selectivity towards 2-methoxy-2-phenylethanol (**2a**) was achieved in 1 h. Product **3a** was also observed in 7% selectivity and its yield grows along the reaction time indicating that **3a** is a secondary product derived from **2a**. When the reaction was performed in the presence of 0.1 mL of pyridine, only 2% conversion of **1a** was observed indicating the poisoning of acid sites present in GO (Table 1, entry 4). It has to be stressed here that the substrate to catalyst ratio used in the present study is 5 mg of GO *versus* 1 mL of **1a** that corresponds to a significantly lower amount of catalyst than that employed for the oxidation of benzyl alcohol (200 wt%)[16] and even hydration of propylene oxide (0.1 g for 50 mmol).[18] The temporal conversion profile of the ring epoxides methanolysis of **1a** is given in Fig. 1. These encouraging results allowed us to reduce the catalyst–substrate ratio further to determine the minimum productivity of GO for the conversion of **1a** by carrying out the reaction in methanol with 3 mL of **1a** and 2 mg of GO. At 1 h reaction time, 69% of **1a** was converted to **2a** with >90% selectivity. After a prolonged time (6 h), the conversion of **1a** was almost complete without much decrease in the selectivity of product **2a**.

Reproducibility of the catalytic activity was checked by performing the same reaction with a different GO batch and its temporal profile is also shown in Fig. 1 giving a visual indication of the data reproducibility. Although the catalyst exhibited slightly higher initial reaction rate, the final conversion and selectivity towards **2a** remained the same. These minor differences in the catalytic activity should be related to differences in the sulfur content (see ESI†). The catalytic activity of GO was much higher than that of Norit A activated carbon that resulted in only 5% conversion of **1a**. In order to assess the active sites present in GO, some control experiments were performed comparing the activity of GO with those of concentrated sulfuric acid, *p*-toluenesulfonic acid and glacial acetic acid. The ring opening of **1a** with methanol was more facile with the former two acids while the carboxylic acid was unreactive and only the unreacted starting material was isolated. This clearly indicates that the active sites of GO are not carboxylic groups, but most probably some hydrogen sulfate acid groups introduced on the GO scaffold during its synthesis. This is further evidenced from the elemental analysis that shows 1.16 wt% of sulfur atoms. To support this proposal, we submitted the as prepared GO to thermal treatment at 200 °C. It is known that mild heat tends to reconstitute graphene from GO and this effects the removal of some groups. Chemical analysis after this treatment indicated that now the sulfur content of the partially reconstituted GO is negligible. The catalytic activity for the ring opening of this partially reconstituted GO was also negligible, supporting the hypothesis that the catalytic activity for this reaction is associated with the presence of sulfur atoms.

To verify whether or not the catalysis is truly heterogeneous or is due to some leached active species present in the liquid phase, the reaction was carried out under the optimized conditions described in Table 1 and the GO solid catalyst was filtered from the reaction mixture at 55% formation of **2a**. After removal of the GO catalyst, the solution in the absence of the solid was again stirred at room temperature. After 1 h, in the absence of the solid no further product formation was observed. Hence, it can be concluded that catalysis occurs on the surface of GO and the process is truly heterogeneous. The reusability of GO was investigated for the ring opening reaction of **1a** with methanol under identical conditions as described in Table 1. After the required time, the solid GO was separated from the reaction mixture by centrifugation at 15 000 rpm and the recovered solid was used without any further treatment. After three consecutive reuses, GO exhibited almost identical catalytic activity. We notice, however, that recycled GO exhibits a little bit higher selectivity towards **2a** due to the decrease in the formation percentage of **3a**. Since **3a** is a secondary product derived from **2a** by acid promoted exchange of the primary hydroxyl group by a methoxy substituent, we suggest that a minor decrease in the acid strength of GO upon reuse is beneficial for **2a** selectivity by minimizing the nucleophilic substitution of the primary hydroxyl group that should require stronger acidity than the epoxide ring opening. Also, no noticeable changes were observed in Raman and XPS analyses after catalysis compared to fresh GO (Fig. S2 and S3, ESI†).

Information about the nature of acid sites and their interaction with probe molecules can be obtained by IR spectroscopy. After activation of the sample at 100 °C in vacuum (10^{-6} mbar) (Fig. 2a) functional groups such as carbonyl groups (1733 cm^{-1}) and sulfate groups (1054 cm^{-1}, SO_3–H stretching) are observed.[19] The band at 1577 cm^{-1} is associated with the C sp^2 vibration of the graphene lattice. Methanol adsorption on the sample at 100 °C leads to a shift of the 1054 cm^{-1} band towards higher wavenumber (1094 cm^{-1}) (Fig. 2b). This shift may be related to the formation of CH_3^+ ions from CH_3OH interacting with the sulfate group ($SO_3^-CH_3^+$). Indeed, the band at 1054 cm^{-1} is restored after

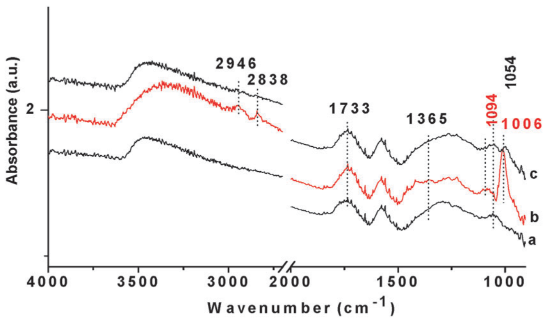
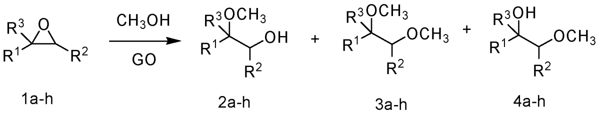
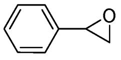
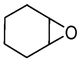
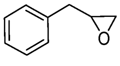
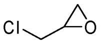
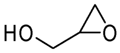
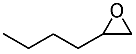
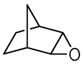


Fig. 2 IR spectra of the sample after 100 °C vacuum activation (a); after evacuation at 100 °C, and admission of methanol at 36 mbar for 5 min (b); followed by evacuation under vacuum at 100 °C (c).

Table 2 Ring opening of epoxides with various substrates catalyzed by GO with different nucleophiles[a]



Run	Substrate	Time/h	Conv.[b] (%)	Product selectivity[b] (%) 2a	3a	4a
1	 1a	1	99	93	7	—
2		1	70[c]	99	—	—
3		3	97[c]	97	3	—
4		1	60[d]	92	8	—
5		3	96[d]	89	11	—
6	 1b	17	12[e]	99	—	—
7		1	43	97	3	—
8		3	50	97	3	—
9		18	60	96	4	—
10		24	62	95	5	—
11	 1c	1	5	14	—	86
12		3	12	15	—	85
13		18	35	17	—	83
14		24	41	21	—	79
15	 1d	24	7	—	—	99
16	 1e	24	42	24	—	76
17	 1f	1	14	43	—	57
18		5	26	44	—	56
19		28	34	45	—	55
20	 1g	1	95	97	—	3
21	 1h	28	12	99	—	—

[a] Reaction conditions: substrate (1 mL), alcohol (10 mL), GO (5 mg), room temperature. [b] Determined by GC. [c] Using ethanol as a nucleophile. [d] Using 1-propanol as a nucleophile. [e] Using *t*-butanol as a nucleophile.

removal of the methoxy group (Fig. 2c). On the other hand, bands at 1006 cm^{-1}, associated with a C–O stretching, and at 2946 and 2838 cm^{-1}, associated with C–H stretching vibration of the methoxy group, are also observed upon adsorption of CH_3OH (Fig. 2b). These spectroscopic changes prove the acidity of the GO obtained by the conventional Hummers oxidation of graphite.

After optimizing the reaction of ring opening of epoxides with **1a** using methanol as a nucleophile, we wanted to study the effect of other alcohols such as ethanol, 1-propanol and *t*-butanol as nucleophiles. As shown in Table 2, methanol exhibited higher reaction rate than ethanol and 1-propanol. Particularly **1a** showed very low conversion with *t*-butanol, this may be due to the steric hindrance caused by methyl groups and a similar reactivity has been reported earlier with other solid acids including MOFs as heterogeneous catalysts.[20] It has to be mentioned here that all the alcohols resulted selectively in a single regioisomer, **1b**, in the presence of GO as catalyst. The methanolysis of cyclohexene oxide resulted in 62% conversion in 24 h to 2-methoxycyclohexanol, **2b**, in 95% selectivity. Interestingly, 2-benzyloxirane showed both isomers, **2c** and **4c**, although the formation of the secondary alcohol is favoured over the primary alcohol.

Epichlorohydrin, **1d**, gave only one isomer with low conversion while glycidol, **1e**, resulted in both isomers in 42% conversion. Then, 1-hexene oxide, **1f**, was also subjected to ring opening of epoxides using methanol as solvent and it was found that both isomers were formed in equal amounts in 28 h. Norbornene oxide, **1h**, also exhibited low conversion even after a prolonged time.

To differentiate between S_N1 and S_N2 reaction mechanisms, 1,2-epoxy-2-methylpropane, **1g**, was selected as a substrate and the nucleophilic ring opening of this epoxide was carried out with methanol. Formation of the less-substituted alcohol as the major product over the more-substituted regioisomer clearly indicates that the reaction is likely to occur through a S_N1 mechanism.

In conclusion, we report a simple and efficient general procedure for the room temperature epoxide ring opening using GO resulting from Hummers oxidation of graphite. Steric encumbrance on the alcohol or impeded diffusion plays an unfavorable role in the conversion of epoxides. The regioselectivity in most of the cases was high, rendering the product expected from an acid catalyzed S_N1 ring-opening mechanism. The catalyst could be easily recovered after the reaction and reused for additional runs before deactivation of the catalyst. The available analytical data and control experiments suggest that the small sulfation occurring during the oxidation protocol introduces sufficient acidity, which combined with the high solubility of GO in water and alcohols and the availability of the active sites located on a 2D surface make the material highly active as an acid catalyst.

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