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Preparation of Manganese/Graphite Oxide Composite Using Permanganate and Graphite: Application as Catalyst in Bromination of Hydrocarbons

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Preparation of manganese/graphite oxide composite using permanganate and graphite: application as catalyst in bromination of hydrocarbons

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Abstract

A highly efficient one-pot preparation of manganese/graphite oxide (MnO_X/GO) composite from graphite and $KMnO_4$ was described. Hummers' preparation method of GO requires a stoichiometric amount of $KMnO_4$, as a result, the method produces a large amount of reduced Mn species. The Mn residue generally is a waste, therefore, we envisioned converting it to value-added materials. A MnO_X/GO composite was prepared in one-pot by treating the unpurified GO with aqueous KOH. The composite was characterized by XRD, XAFS, SEM and TEM. Among various application of the MnO_X/GO composite, we applied as a recyclable catalyst for bromination of saturated hydrocarbons, one of the most basic but important chemical transformations. The MnO_X/GO composite is expected to be an efficient catalyst because of the high surface area and high accessibility of substrates derived from the 2-dimensional sheet structure. When the reaction of a saturated hydrocarbon and Br_2 in the presence of catalytic amount of $MnOx$/GO was performed under fluorescent light-irradiation, a brominated product was formed in high yield in a short reaction time. GO could strongly bind with Mn to prevent elution to the liquid phase, enabling the high recyclability.

1. Introduction

Graphite oxide (GO) has high surface area, good dispersibility, mechanical stability, and a number of oxygen-containing functional groups on the plane and edges of a graphene sheet [1,2]. Because of the attractive chemical and physical properties, the application of GO has expanded from material sciences to biological sciences [3–10]. To improve the performance of GO, composites with metals have been investigated [3,11]. Here, we focused on a facile approach to MnO_X/GO composites. MnO_X/GO composites have been prepared by the hydrothermal method [12–15] using a Mn salt and GO, and have subsequently been used as a catalyst [16], lithium-ion battery electrodes [17, 18], and supercapacitor electrodes [19–24]. We conceived the idea for more efficient preparation of MnO_X/GO when we prepared GO by Hummer's method [25]. The method requires a stoichiometric amount of $KMnO_4$ to oxidize graphite, and produces a large amount of Mn salt as a byproduct. Such Mn salt can be transformed to nanoparticles (NPs) by treating with a base.

Among various application of metal/GO composites, we focused on catalysis in organic synthesis, which has been extensively studied within the past few years [26–31]. One of the most important catalytic reactions is the direct transformation of simple hydrocarbons to value-added chemicals. Organic bromides are valuable compounds, since they have been widely used as starting materials and intermediates in organic synthesis. In the conventional method, organic bromides are synthesized from the corresponding alcohols with HBr [32], PBr_3 [33], or other brominating reagents [34–37]. Although they can be synthesized from corresponding hydrocarbons using high temperature treatment [38], photo irradiation [39], stoichiometric amount of additives [40–42], and catalysts [43], no practical method to meet the requirements of selectivity and efficiency has been proposed. We previously reported that Li_2MnO_3 showed superior performance than conventional methods in the bromination of hydrocarbons [44], however, the reaction still required 10 mol% loading of the catalyst due to the low surface area of the catalyst. Because of the high surface area and high accessibility of substrates derived from the 2-dimensional sheet and nanoparticle structure, the MnO_X/GO composite is expected to be a much more efficient catalyst.

2. Experimental

2.1. Materials

Graphite (SP-1 grade) was purchased from BAY CARBON Inc. $KMnO_4$, Br_2, hexane, benzene, and toluene were purchased from Wako Pure Chemical Industries, Ltd. Cyclohexane was purchased from Nacalai Tesque, Inc. Cyclooctane was purchased from Aldrich Chemical Co. Adamantane and *N*-bromosuccinimide were purchased from Tokyo Chemical Industries Co., Ltd. These materials were used as received.

2.2. Methods

X-ray diffraction (XRD) was measured by PANalytical X' Pert-ProMPD using Cu Kα radiation. X-ray absorption near-edge structure (XANES) data were collected using beamline BL14B2 at SPring-8. Commercially available MnO_2, Mn_2O_3, Mn_3O_4, MnO and $MnBr_2$ were measured as standard samples. Data were analyzed with the Athena software program. Nuclear magnetic resonance (NMR) spectra were recorded using a

Varian NMR System 600 spectrometer. Transmission electron microscope (TEM) images were recorded using a JEOL JEM-2100F and collected from sample powder dispersed on a carbon-coated copper grid. Scanning electron microscope (SEM) images were obtained using a JEOL JSM-IT100 by dispersing the sample on a silicon wafer. Energy dispersive X-ray spectroscopic (EDS) measurements were performed on a SEM (JEOL JSM-IT100) equipped with an energy dispersive X-ray analyzer.

2.3. Preparation of manganese/graphite oxide (MnO_X/GO) composite

To a dispersion of graphite (3.0 g) in 95% H_2SO_4 (75 mL) was slowly added $KMnO_4$ (9.0 g) at <10 ˚C, and the reaction mixture was stirred at 35 ˚C for 2 h. The resulting mixture was diluted by water (75 mL) under vigorous stirring and cooling so that temperature does not exceed 50 ˚C. After 30 min, the suspension was transferred to a centrifuge tube with additional water (40 mL) and centrifuged. After removing the 140 mL of supernatant, water (100 mL) was added. To a part of the suspension (10 mL) was slowly added aqueous KOH (3 M, 30 mL) at 0 ˚C, and the mixture was stirred at room temperature for a few minutes under air. The MnO_X/GO was filtered off and washed with excess H_2O, followed by drying under vacuum.

2.4. General procedure for bromination of hydrocarbons with MnO_X/GO

To a solution of MnO_X/GO (2.00 mg, Mn: 0.011 mmol) in a hydrocarbon was added Br_2 (1.00 mmol) at room temperature, and the reaction mixture was stirred at 80 ˚C for 1 h under air with fluorescent light-irradiation. To this was added dodecane (227 μL, 1.00 mmol) as an internal standard, diluted with ethyl acetate, and the product yield was determined by GC.

2.5. Procedure for catalyst recycling

After completion of the reaction, aqueous KOH (2 M, 0.75 mL) was added and stirred for 5 min. The catalyst was filtered off and washed with H_2O and ethyl acetate, followed by drying under vacuum. The catalyst could be directly used in the next cycle under the same reaction conditions.

3. Results and Discussion

Gao, Qiu and co-workers have reported efficient synthesis methods of MnOx/GO composites using residual Mn of Hummers' method [23, 24 , 45, 46]. Our method is similar to their concept, but more simplified. Graphite was treated with $KMnO_4$ in sulfuric acid at 35 °C for 2 h, where graphite was oxidized and Mn was reduced, and then water was added. In the conventional Hummers' method for the preparation of GO [25], H_2O_2 is added at this stage to remove the residual Mn. In contrast, we added aqueous KOH to precipitate Mn NPs on GO. Atomic absorption analysis revealed that 30 wt% of Mn was contained in the MnO_X/GO, which corresponds to the incorporation of 70% of Mn from $KMnO_4$ used for the oxidation of graphite [47]. The amount of Mn on GO could be reduced to 10 wt% by partially removing the residual Mn by centrifugation before the addition of aqueous KOH.

As prepared MnO_X/GO was characterized by XRD (Fig 1a). A peak at 2θ = 11.0° corresponds to GO (002), and other peaks were completely consistent with Mn_3O_4 (Fig 1d). However, the XANES spectra of the MnO_X/GO (Fig 2Aa) was different from those of pure Mn_3O_4 (Fig 2Ac) and other manganese oxides (Fig 2Ab, 2Ad, 2Ae). We assumed that some of Mn in the MnO_X/GO were crystalline Mn_3O_4, and others were amorphous or ionic Mn species. The oxidation state of Mn in MnO_X/GO was determined to be +3.0 by XANES analysis (Fig S1). Mn was uniformly distributed on GO, as determined by elemental mapping using SEM-EDS (Fig 3). The nanostructure of the MnO_X/GO was observed by TEM (Fig S3a).

We applied the MnO_X/GO composite to the direct bromination of hydrocarbons. The reaction of cyclohexane (**1a**) with bromine in the presence of catalytic MnO_X/GO proceeded to afford the mono-brominated product **2a** in 83% yield (Scheme 1). The recovered catalyst was analyzed by TEM, SEM, and XRD. Consequently, Mn NPs were not observed (Fig S3b, S5a), and no peak of Mn_3O_4 was observed by XRD (Fig 1b). However, we confirmed by atomic absorption analysis that little Mn was eluted into the reaction media, and SEM-EDS analysis also revealed that Mn remained on GO (Fig S5d). In a previous report, Mn oxide was transformed into $MnBr_2$ under similar reaction conditions [44]. SEM-EDS measurement of the recovered MnO_X/GO catalyst showed the uniform distribution of Mn and Br, which supports the formation of a Mn-Br bond (Fig S5). To determine the structure of Mn of the recovered catalyst, XANES analysis was again performed, however, the spectrum was not consistent with $MnBr_2$ (Fig 2Ba, 2Bc), and the average oxidation state of Mn became +2.8 (Fig S1). Therefore, we speculate that the Mn is connected to Br and oxygen functional groups of GO, which prevented the elution of Mn from GO surface. To regenerate Mn NPs, the catalyst was treated again with aqueous KOH, as a result, the XRD pattern recovered and the pattern was consistent with that of Mn_3O_4/GO (Fig 1c). TEM and SEM analysis also confirmed the recovery of Mn NPs (Fig S3, S6). XANES analysis revealed that KOH treatment changed the oxidation state of Mn from +2.8 to +3.5 (Fig 2Bb, S1).

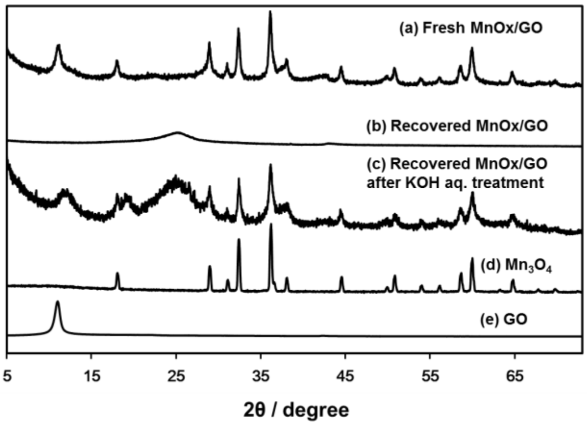


Figure 1. XRD patterns of (a) fresh MnO_X/GO, (b) recovered MnO_X/GO, (c) recovered MnO_X/GO after KOH treatment, (d) Mn_3O_4, and (e) GO.

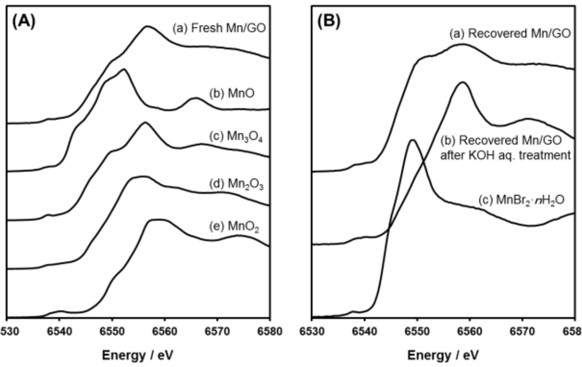


Figure 2. Mn K-edge XANES spectra of (A) (a) fresh MnO_X/GO, (b) MnO, (c) Mn_3O_4, (d) Mn_2O_3, (e) MnO_2; (B) (a)

recovered MnO_X/GO, (b) recovered MnO_X/GO after KOH treatment, and (c) $MnBr_2 \cdot nH_2O$.

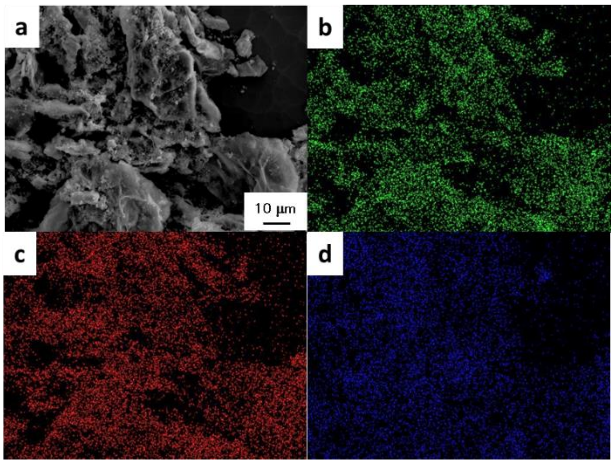
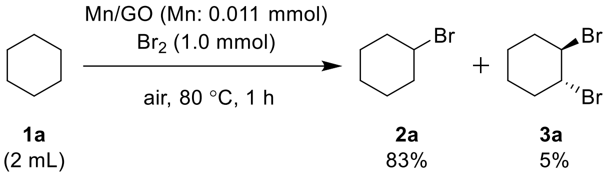


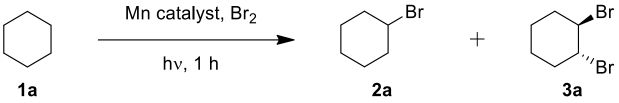
Figure 3. Micrographs of fresh MnOx/GO composite. (a) SEM image, and elemental distribution of (b) carbon, (c) oxygen, and (d) manganese.



Scheme 1. Direct bromination of cyclohexane.

To optimize the bromination conditions, we investigated the reaction temperature, atmosphere. It was reported that the Br_2 is activated on the Mn surface by light [42, 44], therefore, we also evaluated the effect of light. When the reaction was performed at 80 °C for 1 h under air and fluorescent light-irradiation, **2a** and *trans*-1,2-dibromocyclohexane (**3a**) were formed in 66% and 6% yields, respectively (Table 1, entry 1). In contrast, lowering the temperature to 60 °C afforded **2a** in only 20% yield (Table 1, entry 2). The product yield was decreased under an Ar atmosphere, but an oxygen atmosphere did not have any positive effect on the reaction (Table 1, entries 3 and 4). Light was important for the reaction (Table 1, entry 5), because activation of Br_2 requires light of 380–500 nm wavelength [48]. When the ratio of **1a** with bromine was increased, the yield of **2a** increased to 83% and formation of **3a** was suppressed (Table 1, entry 6). For comparison, other bulky Mn oxides, such as Mn_3O_4 (29 µm), MnO_2 (1.9 µm), Mn_2O_3 (1.2 µm), and MnO (5.9 µm), were used as a catalyst, but product yields were low (Table 1, entry 7, and Table S2). When $MnBr_2/GO$, prepared from $MnBr_2$ and GO by evaporation to dryness method, and MnO_x/GO treated by HBr or Br_2 were used as catalysts, the product yields were only 27%, 6%, and 18%, respectively (Table 1, entries 8-10). These results suggest that Mn should not be large particles, and Mn-Br structure is not preferred. Free radical bromination without any catalyst proceeded under light irradiation, but the yield and selectivity were low (Table 1, entry 11).

Table 1. Optimization studies.[a]

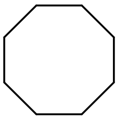
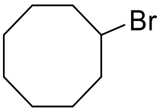
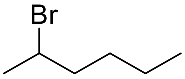
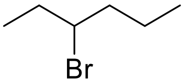
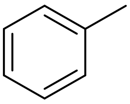
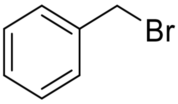
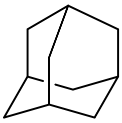
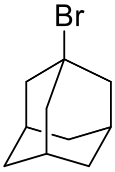
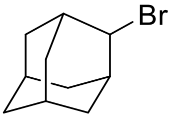
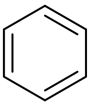
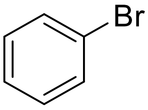


Entry	Mn catalyst	Conditions	Yield (%) [b]	
			2	**3**
1	MnO_X/GO	hv, 80 °C, air	66	6
2	MnO_X/GO	hv, 60 °C, air	20	< 1
3	MnO_X/GO	hv, 80 °C, Ar	49	3
4	MnO_X/GO	hv, 80 °C, O_2	66	7
5	MnO_X/GO	dark, 80 °C, air	N.D.	N.D.
6 [c]	MnO_X/GO	hv, 80 °C, air	83	5
7	Mn_3O_4	hv, 80 °C, air	5	< 1
8	$MnBr_2/GO$	hv, 80 °C, air	27	1
9	MnO_X/GO-HBr	hv, 80 °C, air	6	1
10	MnO_X/GO-Br_2	hv, 80 °C, air	18	1
11	None	hv, 80 °C, air	11	7

[a] All reactions were performed using 1.0 mL of cyclohexane (**1a**), 0.052 mL (1.0 mmol) of Br_2, and 2.0 mg of MnO_X/GO (Mn: 0.011 mmol) at 80 °C for 1 h under air with fluorescent light-irradiation. [b] Yields were determined based on the moles of Br_2 by GC using *n*-dodecane as an internal standard. [c] The reaction was performed using 2.0 mL of **1a**., N.D. = Not Detected.

We next investigated the substrate scope (Table 2). Cyclooctane (**1b**), *n*-hexane (**1c**) and toluene (**1d**) were successfully brominated in high yield in a short reaction time (Table 2, entries 1–3). In contrast, this catalytic system was not suitable for sterically hindered substrates such as adamantane (**1e**) (Table 2, entry 4). Bromination of benzene (**1f**) did not proceed at all (Table 2, entry 5). When **1d** was used, only the benzyl position was brominated (Table 2, entry 3). These results suggest that the reaction passes through a radical intermediate, because bromination of aromatic moiety proceeds via electrophilic substitution with cationic bromine intermediate.

Table 2. Scope of substrates for MnO_X/GO-catalyzed bromination.[a]

Entry	Substrate	Time	Product [b]	
1	 **1b**	10 min	 **2b**	92%
2	 **1c**	10 min	 **2c**	 **2c’**
			75% (**2c** : **2c’** = 1.6 : 1) [c]	
3	 **1d**	2 min	 **2d**	98%
4 [d]	 **1e**	24 h	 **2e** 11%	 **2e’** 4%
5	 **1f**	2 h	 **2f**	< 1%

[a] All reactions were performed using 2.0 mL of **1**, 0.052 mL (1.0 mmol) of Br_2, and 2.0 mg of MnO_X/GO (Mn: 0.011 mmol) at 80 °C under air with fluorescent light-irradiation. [b] Yields were determined based on the moles of Br_2 by GC using *n*-dodecane as an internal standard. [c] The product ratio was determined by ^{1}H NMR. [d] **1e** was used in 2.0 equiv. of Br_2 and $CHCl_2CHCl_2$ (2 mL) as a solvent.

Finally, we explored the reusability of MnO_X/GO in the bromination of **1a**. After completion of the reaction, aqueous KOH was added before product yield was determined by GC. The catalyst was recovered by filtration and washed with H_2O and ethyl acetate, followed by drying under vacuum. The catalyst could be directly used in the next recycle under the same reaction conditions. The yields of **2a** and **3a** were almost consistent for five cycles without leaching Mn in the liquid phase (Fig 4).

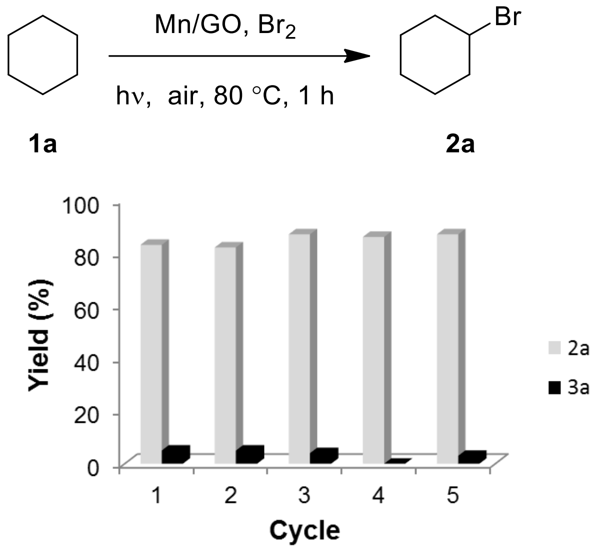


Figure 4. Recycle experiment after treating the catalyst with aqueous KOH.

4. Conclusion

In conclusion, we have successfully developed a facile preparation method for MnO_X/GO composites from graphite and $KMnO_4$. The MnO_X/GO could be applied as a catalyst for direct bromination of hydrocarbons. The catalyst could be reused by treating with aqueous KOH to remove Br from Mn species. GO could strongly bind with Mn to prevent elution to the liquid phase; therefore, we expect that the MnO_X/GO composite can be applicable not only in the catalysis, but in a wide range of areas such as electrode materials.

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Graphical Abstract

<Title>
Preparation of manganese/graphite oxide composite using permanganate and graphite: application as catalyst in bromination of hydrocarbons

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<Summary>
Manganese (Mn) /graphite oxide (GO) composites were prepared in one-pot by oxidizing graphite with $KMnO_4$ (Hummers' method) and successive treatment with KOH aq. The Mn/GO was applied as a recyclable catalyst for bromination of hydrocarbons, one of the most basic but important chemical transformations.

<Diagram>