



Aerobic oxidation of cyclohexane catalyzed by graphene oxide: Effects of surface structure and functionalization

Yepeng Xiao, Jincheng Liu*, Kaihong Xie, Weibin Wang, Yanxiong Fang*

School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China

ARTICLE INFO

Article history:

Received 27 June 2016

Received in revised form 12 January 2017

Accepted 13 January 2017

Keywords:

Graphene oxide

Nano graphene oxide

Reduction

Cyclohexane oxidation

Surface functionalization

ABSTRACT

Despite extensive development efforts on new catalysts for cyclohexane oxidation, current commercial processes are still desirable to further decrease the economic and environmental costs in the oxidation procedures. In this study, the catalyst properties of metal-free functionalized graphene oxide (GO) in the selective oxidation of cyclohexane is investigated to understand the effects of structure, functional groups and oxygen-containing groups. Both GO sheets and nano graphene oxide (NGO) sheets possess high cyclohexane conversions of 16.7% and 17.7% comparable to that of metal catalysts in the aerobic oxidation of cyclohexane. The higher catalytic activity of NGO sheets is caused by the smaller size and the higher content of –COOH. Within the oxygen-containing groups, the carboxylic acid groups on the surfaces of GO are supposed as the active site for the generation of $\cdot\text{O}_2^-$ radical, which is the active oxygen species in this catalytic oxidation process.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Catalytic oxidation of cyclohexane (CyH) to a mixture of cyclohexanone and cyclohexanol (KA oil), which is one of the most challenging reactions among partial oxidation of the relatively inert C–H bond of alkanes [1,2], becomes increasingly important due to the great need of these products as precursors in the nylon-6 and nylon-6,6 polymers synthesis [3]. Recyclable catalysts with high stability and activity are still highly desirable to further decrease the economic and environmental costs in the oxidation processes. The ideal catalytic oxidation process would use a recyclable and inexpensive catalyst in solvent-free or nontoxic solvents with good conversion and selectivity in the dry air or molecular oxygen as the only oxygen source. Recently, the transitional metal catalysts on the large surface supports or porphyrins are widely utilized in the catalytic cyclohexane oxidation [4–7]. However, drawbacks such as unsatisfactory activities, harsh reaction conditions, sensitivity to air or water, the high cost and the detrimental effects of toxic metal significantly limited its further applications with these metal-based catalysts [8,9]. Hence, it is highly desirable to design a recyclable catalyst that is cheap, metal- and solvent-free, easy-to-handle and highly efficient for the catalytic oxidation of cyclohexane.

Notably, carbon-based materials are considered as promising catalysts because of their low cost, environmental friendliness, high catalytic selectivity and good durability. Carbon or carbon-based materials such as graphene (G) [10,11], carbon nanotubes (CNTs) [12,13], carbon quantum dots (CQDs) [14] and graphitic carbon nitride (g-C₃N₄) [8,15] have received increasing attention as metal-free heterogeneous catalysts owing to their environmental compatibility, outstanding thermal and chemical stability and large surface area. Moreover, carbon materials normally exhibit significant advantages in activity by structure modification [11] (e.g. heteroatom doping) and surface functionalization [16]. In particular, dopants in the carbon skeleton play important roles in tuning the electronic characteristics. The enhancement of oxidation of saturated C–H bonds catalytic activity by doping could be summarized that the dopants break the electroneutrality of sp² carbon and induce changes of both atomic charge and spin density to create charged sites favorable for facilitating the adsorption of O₂ and reactive intermediates no matter the dopants are electron-rich or electron-deficient [17]. On the other hand, it is well-known that the functionalization of carbon or carbon-based materials makes them excellent supports to anchor inorganic nanocrystals with good dispersion and stability [18]. Besides, surface functional groups play significant roles in some reactions. In gas-phase oxidative dehydrogenation (ODH) reactions, the catalytic cycle starts with the activation and dehydrogenation of hydrocarbons at quinone sites, and ends with the re-activation of carbon by oxygen [13]. Carboxylic acid groups on the surfaces of carbon catalysts are identified

* Corresponding authors.

E-mail addresses: JCLIU@gdut.edu.cn (J. Liu), fangyx@gdut.edu.cn (Y. Fang).

as the active sites for the wet air oxidation of phenol [19]. However, so far, the mechanistic reason of carbon catalysis in most liquid-phase reactions has not been rationalized in liquid-phase oxidative catalysis clearly.

In this work, the effect of the oxygen-containing groups of graphene oxide (GO) in the catalytic oxidation of cyclohexane has been discovered during the investigation on the catalytic activity of GO and GO with various surface modifications. Nano-GO (NGO) sheet behaves surpassing activity than that from the big GO sheets. An increased conversion of cyclohexane has been obtained with a higher oxygen-containing GO, and reduced GO (r-GO) has inferior activity. Moreover, the carboxylic acid functionalization seems to benefit the reaction, but a sulfonic acid functionalized GO (GO-SO₃H) shows not much different compare to the counterpart of r-GO. It is implied that a certain amount and a certain type of oxygen-containing of GO plays a indispensable role in the catalytic oxidation of cyclohexane.

2. Experimental

2.1. Materials

Natural graphite was purchased from Bay Carbon Company, USA. Sodium nitrate (NaNO₃, 99%), potassium permanganate (KMnO₄, 99%), hydrogen peroxide (H₂O₂, 35%), concentrated sulfuric acid (98%), acetone, ClCH₂COONa, ClCH₂CH₂SO₃Na, triphenylphosphine (PPh₃, 99%) and benzoyl peroxide (BP) were purchased from Aladdin, China. All reagents were used without further purification.

2.2. Synthesis of GO, NGO, GO-COOH, GO-SO₃H and r-GO

GO was synthesized by a modified Hummers method [20]. The GO-COOH and GO-SO₃H was produced by a bath sonication process [21,22]. Briefly, 20 mg of GO, 1000 mg of ClCH₂COONa (or BrCH₂CH₂SO₃Na) and a certain amount of NaOH were added into 50 mL of DI water, and the mixed solution was sonicated for 0.5, 1, 2, 5 h, respectively. The as-prepared GO-COOH (or GO-SO₃H) was neutralized by HNO₃ and purified by DI water twice.

The r-GO was produced by a simple bath sonication process. Typically, 20 mg of GO with 100, 200 and 400 mg of NaOH were added into 50 mL of DI water, and the mixed solution was sonicated for 0.5, 1, 2 and 5 h (marked as r-GO-100 mg-0.5 h etc.), respectively. The as-prepared r-GO was neutralized by HNO₃ and purified by DI water twice. Meanwhile, NGO sheets prepared by refluxing 40 mg of GO in 5 mol/L solution of HNO₃ for 72 h was used for comparison.

2.3. Characterization

Transmission electron microscopy (TEM) images were obtained using a JEM-2100 microscope. Atomic force microscopy (AFM) was carried out using a non-contact mode on a PSIA XE-100 scanning probe microscope. X-ray powder diffraction (XRD) patterns were operated on a Ultima III using Cu K α irradiation. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Perkin Elmer GX FT-IR system. X-ray photoelectron spectroscopy (XPS) measurements were carried out by using a Kratos Axis Ultra Spectrometer. The UV-vis absorption spectra were recorded by using an Evolution 300 spectrophotometer.

2.4. Typical oxidation procedures

The cyclohexane oxidation reaction was performed in a Teflon-lined 100 mL stainless-steel autoclave equipped with a magnetic stirrer. 43.5 mmol of cyclohexane and 20 mg of catalyst which was

Table 1
Effect of residual impurities on CyH oxidation.

Catalyst.	Conversion (%)	K/A ^c	Selectivity ^d (%)			
			KA	CHHP	AA	Others
GO	16.7	1.4	45.2	3.0	46.3	5.5
DI-GO ^a	16.6	1.4	44.0	2.2	48.0	5.8
GO (0.5 wt%Mn) ^b	16.2	1.4	44.1	2.4	47.7	5.8

^a DI-GO: GO after an ion exchange processing in DI water at room temperature for 7 days.

^b As-prepared GO acetic suspensions with 0.5 mg MnSO₄.

^c Molar ratio of cyclohexanone to cyclohexanol.

^d Selectivity of major products after 8 h reaction. KA: cyclohexanone and cyclohexanol, CHHP: cyclohexyl hydroperoxide, AA: adipic acid, the others included glutaric acid, succinic acid, hydroxyl hexylic acid and ϵ -caprolactone and other undetected acids.

dispersed in 5 mL of acetone were introduced into the reactor without any initiator. The optimum temperature was set at 140 °C with the air pressure 1.5 MPa initially. After 8 h reaction, the autoclave was removed from oil bath to an ice-water bath and maintained for about 1 h, which was necessary for the system to cool down completely.

For analyzing the products of cyclohexane oxidation, FID gas chromatography (GC, Agilent-7890A, capillary column: HP-5, 30 m \times 0.25 mm, nitrogen as carrier gas with internal standard method, using cyclopentanol as the standard substance) was used for the qualitative analysis. The conversion was calculated based on the starting cyclohexane. Cyclohexyl hydroperoxide (CHHP) contents were determined by decomposition with triphenylphosphine (PPh₃) and quantification of the additionally formed cyclohexanol by GC. Other products including acids and esters were determined by HPLC (Agilent 1260). Additionally, about 95% mass balance was obtained for the reaction based on the initial feeding amount of cyclohexane.

3. Results and discussions

3.1. Characterization

The hydrophilic GO sheets produced by Hummers method have the average size of 1–2 μ m (Fig. 1a). The as-prepared GO can be dispersed well in de-ionized (DI) water, forming a stable yellow-brown suspension (Fig. 1a, inset). Fig. 1b shows the UV-vis absorption spectra of GO, NGO, GO-COOH and GO-SO₃H. The absorption peak at 227 nm corresponding to π - π^* transitions of aromatic C=C bonds [21]. However, the absorption peaks of GO-COOH and GO-SO₃H sheets show a slight red-shift due to the partial removal of oxygen functional groups during the functional processing [23]. As shown in Fig. 1c, the C, O and S photoelectron lines can be detected in the XPS survey spectra of GO. The TEM, UV-vis absorption and XPS analyses confirm the successful synthesis of high-quality GO, GO-COOH and GO-SO₃H sheets.

One of the key concerns in identifying and describing metal-free catalysis is the suspected influence of metal impurities in the catalyst. In order to eliminate the catalytic influence of residual metal ions, all the materials have been suffered to a dialysis process for 1 week before the oxidation experiments. The possible impacts of Mn²⁺ or other impurities that may be introduced during the preparation of GO were investigated by a contrast experiment as Table 1. It can be seen that, the conversion of cyclohexane and the distribution of the reaction products have no evident difference among GO, DI-GO and GO with the addition of 0.5 wt% manganese (Mn) salt. This suggests that the residual Mn metals are not the active site or have negligible effect in the CyH oxidation.

Download English Version:

<https://daneshyari.com/en/article/4751897>

Download Persian Version:

<https://daneshyari.com/article/4751897>

[Daneshyari.com](https://daneshyari.com)