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Co/rGO Synthesized via Alcohol Thermal Methods as Heterogeneous Catalyst for Highly Efficient Oxidation of Ethylbenzene with Oxygen

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Co₃O₄ nanoparticles uniformly dispersed on reduced graphene oxide (Co/rGO) were synthesized by alcohol thermal method as highly efficient catalyst with initiator NHPI for the selective oxidation of ethylbenzene to acetophenone using O2 as green oxidant. X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) were carried out for the chemical, morphological, and size analyses of the nanocomposite. The ensuing catalyst was evaluated for the oxidation of ethylbenzene with high conversion of 84.1% and acetophenone selectivity of 96.2% within only 2 h. Moreover, Co/rGO catalyst showed good recyclability and activity toward the selective oxidation of ethylbenzene. It is revealed that the enhanced catalytic activity of Co/rGO is derived from the interaction of the active center the support material graphene. CO_3O_4 and

Introduction

Selective oxidation of ethylbenzene to useful acetophenone is a significant reaction in the research of organic chemistry and chemical industry, because acetophenone is an important intermediate in the production process of resins, alcohols, aldehydes, esters and pharmaceuticals, and can also be used as solvent for esters, dyestuff and preservatives.^[1-3] Works relating to liquid-phase oxidation of ethylbenzene to acetophenone have been reported using transition-metal (Co, Cu, Fe, etc.) compounds as homogeneous catalysts.^[4,5] However, these catalysts not only are difficult to separate for recovery after oxidation but also encounter decreased catalytic activity due to self-aggregation of active sites,^[6] thus leading to complicated post-processing and a lot of pollution of metal. In order to avoid these problems concerning homogeneous catalysts, it is of great significance to develop more easily-separated, reusable and environmental friendly heterogeneous catalysts for ethylbenzene oxidation, such as MnFeSi,^[7] MnO₂/MgAl-LDH,^[8] Co-N-C/SiO₂,^[9] Au/rGO,^[10] CoZnAl-MMO/Al₂O₃,^[11] and MnOx/HTS.^[6] Among these supported catalysts, graphene-based catalyst has attracted more and more attention of researchers and has been widely used in catalysis field.

Graphene, as a novel two-dimensional carbon material with excellent physical and chemical properties, has been widely researched in catalytic reactions by combining with metal. aromatic alcohols oxidation,^[12,13] C=C bond selective hydrogenation,^[14] nitroarenes hydrogenation,^[15-17] H₂O₂ decomposition^[18-20] and cross

coupling reactions.^[21-23] In these cases, graphene oxide (GO) is frequently used as a precursor for graphene and plays a significant role as support material, since it may contribute to the dispersion of metal particles on the surface of graphene because of the oxygen functional groups (hydroxyl group, epoxy group, carboxyl group)^{[24-^{28]} and accelerate the transfer of electrons due to the large number of carbon-carbon double bonds.^[25-29] In addition, GO can be easily reduced to graphene by chemical reduction, hydrothermal reduction or thermal annealing.^[26,27-29] Based on above, it is widely believed that graphene is a very promising carbon material applied in catalytic reactions, combined with the unique advantages of metal nanoparticles via improving particle dispersion, reducing particle size, exposing more active sites and enhancing stability.}

In consideration of the fact that the alcohol solvet is often adopted as the solvent for the fabrication of metal oxides with uniform size ang morphology, here in our work, nano-sized Co_3O_4 particles supported on reduced graphene oxide (Co/rGO) were prepared via the simple alcohol thermal reaction, during which the glycol adopted as the solvent. Across the alcohol thermal reaction process, all of precursors became active until reaching the supercritical conditions, thus finally leading to the homogeneous reaction solution for the synthesis of the nano-materials. The as synthesized Co/rGO exhibited advanced catalytic activity and reusability for the selective oxidation of ethylbenzene to acetophenone using O_2 as green oxidant in the presence of radical initiator.

Results and Discussion

Characterizations

Fig. 1. showed the power X-ray diffraction patterns of GO, rGO and Co/rGO. The typical diffraction peak (002) was observed at $2\theta = 11^{\circ}$ from GO,^[33] attributed to the oxygen functionalities generated in the interlayer spacing of graphite after oxidation.

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Alone with the reduction, the characteristic peak decreased rapidly in rGO and Co/rGO and appeared around $2\theta = 23.1^{\circ}$ instead, demonstrating that the surface oxygen groups of GO were removed partially in the process of alcohol-heating reducing and conjugated graphene network sp² was reestablished. In addition, Co/rGO catalyst exhibited new diffraction peaks at $2\theta = 18.4^{\circ}$, 36.9° , 44.2° and 59.8° , which correspond to the Co (111), (311), (400) and (511) crystal planes of cubic Co₃O₄.^[34] These results suggest that the Co₃O₄ nanoparticles was successfully modified on the surface of rGO.



Figure 1. XRD patterns of GO, rGO and Co/rGO.

TEM and SEM images of Co/rGO are presented in Fig. 2. It can be seen that Co_3O_4 nanoparticles with a size distribution in the 11-34 nm range (average diameter 23 nm) are uniformly deposited on the transparent rGO sheets with crumpling (Fig.2, (b)), and it is well consistent with SEM observations (Fig. 2, (d)). Moreover, we found that particles are mainly distributed on the edge of rGO without obvious agglomeration and the thin sheet structure and wrinkles of GO (Fig. 2, (a) and (c)) are retained after reduction treatment.



Figure 2. (a) TEM images of rGO. (b) TEM images of Co/rGO and the particle size of the Co_3O_4 nanoparticles on rGO. (c) SEM images of rGO. (d) SEM images of Co/rGO.

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The XPS spectrum is shown in Fig. 3 to quitter analyze the surface elemental composition of the Co/rGO nanocomposite. The full survey spectra (Fig. 3, (a)) displays the existence of C, O, Co elements without other impurities. The peak of O 1s might stem from the residual oxygen of rGO and the peak of Co 2p appeared in 800.1 eV. The surface Co amount in the XPS data is 36.5 wt.% and the total Co loading is 35.8 wt.% detected by ICP-OES analysis (Table S1). The tiny variation of cobalt concentration between XPS and ICP-OES is due to the principle differences between the two testing methods, in that the XPS is a surface analysis method, which provide the surface element concentration and the surface chemical state. While, as for ICP-OES, it is a more accurate testing method from which the overall composition was obtained. The XPS spectrum of Co 2p shown in Fig. 3 (b) shows two peaks at binding energies of 781.5 eV and 783.2 eV for $Co^{3+} 2p_{3/2}$ and Co2+ 2p_{3/2}, respectively. The other two peaks assigned to Co $2p_{1/2}$ are detected at 797.2 eV for Co³⁺ cations and 798.5 eV for Co²⁺ cations.^[35] Additionally, the Co²⁺ shakeup satellites of Co₃O₄ are also observed at 787.1 eV and 803.4 eV.^[36]



Catalytic activity for the selective oxidation of ethylbenzene

The activities of Co/rGO catalyst for the selective oxidation of ethylbenzene using O2 were summarized in Table 1. It was clear that the reaction process was difficult to carry out without any catalyst, giving only 2.6% conversion of selectivity, ethylbenzene and 89.1% acetophenone respectively (Table 1, entry 1). Under the same conditions, the Co/rGO exhibited high catalytic performance with 84.1% conversion and 96.2% selectivity (Table 1, entry 3) in the presence of NHPI (hydroxyphthalimide). And GC-MS, HPLC were also use to check the molecular weight of the product, There are only benzoic acid and CO2 side-product, wothout acetophenone acid and other side product. To further explore the effect of support material in the catalytic reaction, a Cofree rGO material reduced by the same method was used to catalyze this reaction and no obvious substrate consumption (only 3.8% conversion) was observed (Table 1, entry 2), which indicated rGO had no catalytic activity for this reaction. Futhermore, different cobalt-based catalysts were investigated for the selective oxidaton reaction. Co/AC (Active carbon) and Co/GP (graphite powder) gave relatively low ethylbenzene conversion (65.5% and 58.3%, respectively) with about 90% acetophenone selectivity (Table 1, entries 4 and 5). The results suggested that the catalytic activity of Co/rGO composites

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originates from Co_3O_4 and rGO as a support can contribute to improve the activity of Co_3O_4 -loaded catalyst. Additionally, different amounts of Co/rGO catalysts (0.5 wt%, 1.0 wt%, 1.5 wt%, 2.0 wt%, 2.5 wt%) for ethylbenzene amount, were applied for the reaction in order to detect the optimum amount for ethylbenzene oxidation. The results revealed that 2.0 wt% of Co/rGO showed higher catalytic activity with increases in catalyst from 0.5 wt% to 2.0 wt% (Table 1, entries 7-10), resulting from the increasement of active sites. Notably, excessive heterogeneous catalysts may cause conversion reduction due to the blocks between the substrate and the oxidant (Table 1, entry 11). It could be also found that only 46.8% ethylbenzene conversion was obtained in the absence of NHPI (Table 1, entry 6), indicating that NHPI plays an important role as a trigger for oxidation of ethylbenzene.

Table	1.	Oxidation	of	ethylbenzene	to	acetophenone	catalyzed	by
differe	nt c	atalysts. ª						

Entry Catalyst		Conv./%	Select./%	
1 ^b	absence	2.6	89.1	
2	rGO	3.8	87.0	
3	Co/rGO	84.1	96.2	
4	Co/AC	65.5	89.7	
5	Co/GP	58.3	90.4	
6 ^c	Co/rGO	46.8	88.5	
7	0.5 wt.% Co/rGO	43.4	89.3	
8	1.0 wt.% Co/rGO	67.5	91.2	
9	1.5 wt.% Co/rGO	79.4	90.5	
10	2.0 wt.% Co/rGO	84.1	96.2	
11	2.5 wt.% Co/rGO	86.0	89.7	

^aReaction conditions: 1 mL ethylbenzene, 2 mL CH₃CN, 6 mol% NHPI (hydroxyphthalimide), 2.0 wt% catalyst, 0.3 MPa O₂, 120 °C, 2 h. ^bCatalyst-free, cNHPI-free.

Inspired by these intriguing results, we optimized the reaction conditions in order to further understand the catalytic performance of Co/rGO, such as the effects of the reaction temperature and reaction time on the conversion of ethylbenzene and the selectivity of acetophenone. The ethylbenzene conversion increased markedly from only 10.4% at 60 °C to 84.1% with the elevated temperature to 120 °C, and the acetophenone selectivity improved by 21.0% from the original 75.2% (Fig. 4, (a)). However, as reaction temperature continued to rise, acetophenone selectivity changed to decrease with slightly increased conversion, indicating that the overoxidized side-product benzoic acid could generate easily at excessive temperature.

Fig. 4 (b) illustrated the relationship between the catalytic
activity of Co/rGO and reaction time. Remarkably, the
ethylbenzene conversion and acetophenone selectivity
increased greatly as reaction time was 2 h. When the reaction

time was extended to 10 h, the selectivity decreased is lightly but the conversion kept at a preferable 1020619 with 1020619 significantly change at the same time.



Figure 4 Oxidation of ethylbenzene at different (a) temperature and (b) time intervals.

For the free radical NHPI initator was introduced in the reaction system, to explore the effect of the solvent in this catalytic reaction, various organic solvents were used in the oxidation of ethylbenzene, such as CH₃COOH, CH₃COOC₂H₅, CH₂Cl₂, DMF, CH₃COCH₃, CICH₂CH₂Cl, CH₃CN and PhCN, and the results were summarized in Table 2. A series of experiments showed that CH₃CN was the best solvent in this oxidation system with 84.1% conversion and 96.2% selectivity (Table 2, entry 2), but CH₃COOH and DMF are the opposite, affording lower ethylbenzene conversion of 34.3% and 35.7%, respectively (Table 2, entries 3 and 4). When the reaction was carried out without solvent, the conversion of ethylbenzene was only 29.5% (Table 2, entry 1). Therefore, CH₃CN as a solvent plays an effective role for the transition of free radical in the oxidation reaction. The above results revealed that these solvents have obvious influences on the activity of Co/rGO for the selective oxidation of ethylbenzene.

Table 2. Oxidation of ethylbenzene in different solvents.^a

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Entry	Solvent	Conv./%	Select./%
1		29.5	91.5
2	CH₃CN	84.1	96.2
3	CH₃COOH	34.3	84.7
4	DMF	35.7	80.8
5	$CH_3COOC_2H_5$	57.9	80.1
6	CH ₃ COCH ₃	55.2	92.0
7	CH_2CI_2	70.1	93.3
8	CICH ₂ CH ₂ CI	61.5	79.8
9	PhCN	59.8	89.1

^a Reaction conditions: 1 mL ethylbenzene, 2 mL solvent, 6 mol% NHPI (hydroxyphthalimide), 2.0 wt% catalyst, 0.3 MPa O₂, 120°C, 2 h.

The effect of different initiators on the oxidation of ethylbenzene has been also studied (Table 3). In the absence of any initiator, 46.8% conversion of ethylbenzene and 88.5% selectivity of acetophenone was obtained over Co/rGO at the catalyzed by Co/rGO (Table 3, entry 1). When the reaction was initiated by dibenzoyl peroxide (BPO) and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), the conversion is

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dropped sharply to 9.2% and 7.4% respectively, but the former gave very low selectivity only 66.2% (Table 3, entries 2 and 3). Azobisisobutyronitrile (AIBN) was use as initiator and showed a mild effect with 51.5% conversion and 91.4% selectivity (Table 3, entry 4). After several contrast experiments, NHPI proved to be the best initiator with 84.1% conversion of ethylbenzene (Table 3, entry 4). The results showed that Co/rGO/NHPI catalytic system could give much higher conversion of ethylbenzene and selectivity for acetophenone compared with the single Co/rGO (Table 3, entry 5).

 $\ensuremath{\text{Table 3.}}$ Oxidation of ethylbenzene catalyzed by Co/rGO using different initiators.ª

Entry	Initiator	Conv./%	Select./%
1		46.8	88.5
2	BPO	9.2	66.2
3	TEMPO	7.4	93.0
4	AIBN	51.5	91.4
5	NHPI	84.1	96.2

^aReaction conditions: 1 mL ethylbenzene, 2 mL CH₃CN, 6 mol% initiator, 2.0 wt% catalyst, 0.3 MPa O_2 , 120°C, 2 h.

The selective aerobic oxidation ethylbenzene to acetophenone has been generally accepted as a radical reaction^[37,38]. Based on the above experimential studies carried out in the absence and presence of Co/rGO catalyst or NHPI, the possible reason may be accounted for the high activity of Co/rGO/NHPI catalysis system. The most important intermediate III, which is originated from ethylbenzene combined with O2, can be accelerated to decompose into to acetophenone by the Co/rGO catalyst in the absence of any initiator and the result is consistent with Table 3 (Entry 1). Besides, NHPI can be converted to reactive phthalimide N-oxyl radical (PINO) in the reaction with O₂, which is able to abstract the hydrogen atom from a saturated carbon of ethylbenzene, forming the corresponding benzylic radical I. Under the oxygen atmosphere, these radicals subsequently react with O_2 to form II, that is further translated into III and ultimately acetophenone, as shown in Fig. 5. In order to facilitate this pathway, Co/rGO catalyst have been utilized and afford desirable results.



Figure 5. Schematic illustration for the catalytic oxidation ethylbenzene to DOI: 10.1039/C9NJ00470J acetophenone by the Co/rGO nanocomposite. The reusability of the heterogeneous catalyst is a definite advantage compared with homogeneous catalyst. The Co/rGO catalyst was reused additional five times under the optimal reaction conditions after separation from the reaction system by filtration, washing and lyophilization and the results were shown in Fig. 6. Only slight decrease was observed in catalytic activity including conversion and selectivity for oxidation of ethylbenzene after several cycles, showing that the catalyst had no overmuch mass loss or deactivation. The X-ray diffraction analysis of the Co/rGO catalyst after used for five consecutive times revealed that the crystal structure of Co nanoparticles anchored on the surface of graphene was not changed. Furthermore, SEM and EDS images (Fig. S2) exhibited that the recycled catalyst maintained the original morphology compared with the catalyst being used before. The results may be associated with the large specific surface area of graphene in favor of the dispersion of metal particles and preventing aggregation.

Ethylbenzene conversion Acetophenone selectivity



Figure 6. Recycling of Co/rGO catalyst for the selective oxidation of ethylbenzene.

Table 4. Comparision merit of the Co/rGO catalysts with other similar catalysts
reported.

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Catalyst	T /ºC	t /h	Conv. /%	Select. /%	Ref.
Al ₂ O ₃ @CoCuAl-MMO	120	12	93	89	[39]
Ag/SiO ₂	120	12	38	88	[40]
N-rGO	80	12	99	92	[41]
LC-N	80	24	98	91	[42]
Ti-Zr-Co	170	4.5	62	69	[43]
Co-N-C/g-C ₃ N ₄	120	5	28	78	[44]
Car-NHPI/NHQI	120	15	70	66	[37]
Co-N-C-S	120	5	17	76	[45]
Fe@CNTS	155	3	37	60	[46]
Co@GCNs	120	5	68	93	[47]
Co/rGO/NHPI	120	2	84	96	This work

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Reported catalysis come from the references. This work reaction conditions: 1 mL ethylbenzene, 2 mL CH₃CN, 6 mol% initiator, 2.0 wt% catalyst, 0.3 MPa O_2 , 120°C, 2 h.

The Co/rGO catalyst presented in this work exhibits advantages in terms of short reaction time, high conversion and selectivity for the selective oxidation of ethylbenzene and the catalytic effects are compared with other similar catalysts reported in literatures [Table 4]. Firstly, graphene (rGO), as a novel two-dimensional carbon material with excellent physical, electrical conductivity and chemical properties, is frequently used as a supporter for transition metal catalysts, which contribute to the dispersion of metal particles via the oxygen functional groups (hydroxyl group, epoxy group, carboxyl group) on the surface of graphene. Secondly, synergistic catalysis from the π - π stacking of the rGO and ethylbenzene plays efficiently bonding role.

Conclusions

In summary, the Co/rGO nanocomposite was synthesized by one-step alcohol thermal method. The obtained Co/rGO catalyst exhibited excellent catalytic activity (84.1% conversion, 96.2% selectivity) in a short time (2 h) for selective oxidation of ethylbenzene to acetophenone. Especially, O_2 as cheaper and cleaner oxidant in the catalytic oxidation reaction makes the catalytic system more practical. The satisfactory catalytic effect is the result of the combined action of highly active graphene-supported Co_3O_4 and free-radical initiator NHPI. Hence, due to their simple preparation, good recyclability, low cost and environmental friendliness of the Co/rGO composites catalysts, it is expected that this work may offer effect catalyst to practical selective oxidation of ethylbenzene to produce acetophenone.

Experimental Section

Synthesis of GO

GO was prepared from graphite powders by the modified Hummers method. Graphite powers (1.0 g), NaNO₃ (1.0 g) and H_2SO_4 (20 mL) were put into a 250 mL flask, and then KMnO₄ (3.0 g) was added slowly under stirring in an ice bath. The reaction system was transferred to a 40 °C water bath and vigorously stirred for about 30 min. Then ultrapure deionized water (50 mL) was slowly added to the solution and stirred for another 30 min at 80 °C. The mixture was poured into 200 mL water and followed by addition of 10 mL H_2O_2 (30%), yielding a yellow suspension of GO. The mixture was filtered and washed with HCl (10%) aqueous solution and the resulting solid was dispersed in 300 mL water. Finally, it was purified by dialysis for one week using a dialysis membrane to remove the remaining acid and metal species. The generated GO aqueous dispersion was stirred for 10 h and sonicated for 30 min to exfoliate it.

Synthesis of Catalysts

The aqueous solutions of GO (8.2 mg·mL⁻¹, 5.0 mL), 120 mg of Co(OAc)₂·H₂O and 60 mg of L-glutamic acid were mixed together in 35 mL of glycol to form a homogeneous suspension

by ultrasound and stirring. Then, the pH value of the tay stem was adjusted to 11-12 by the dropwise addition of the tay stem solution (2 mol·L⁻¹) under vigorous stirring. Above suspension was then transferred into a 50 mL Teflon-lined stainless-steel autoclave followed by thermal treatment at 150 °C for 8 h. After being cooled down to room temperature, the obtained catalyst was collected by centrifugation and throughly washed with 0.1 M KOH and distilled water, and lyophilization was applied to prevent the aggregation of graphene sheets during the drying process. The Co₃O₄ nanoparticles supported on activated carbon (Co/AC) and graphitized carbon (Co/GC) were synthesized by the same method.

Selective oxidation of ethylbenzene

The selective oxidation of ethylbenzene to acetophenone over the synthesized nanocomposite was conducted in a Teflonlined stainless-steel autoclave using O2 as oxidant. Typically, NHPI (N-hydroxyphthalimide) and Co/rGO catalyst were dispersed in acetonitrile (2 mL) and then the etylbenzene (1 mL) was added. After the reactor was sealed, removed air and pressurized with O2, the mixture was heated to 120 °C for 2 h under magnetic stirring. Upon reaction completion, the heterogeneous catalyst was recycled from reaction mixture by filtration and the reaction solution was guantitatively analyzed by an Agilent 7890 series gas chromatograph (GC). And all products were confirmed by GC-MS (Shimadzu GCMS-QP2020) as well as by comparing the retention times to respective standards in GC traces. Agilenft Hypersil ODS column (4.6 \times 250 mm) and UV detector (at 256 nm), was used to analyze the non-gasifiable products (benzoic acid). The eluent was 0.01 mol L⁻¹ KH₂PO₄ in an acetonitrile-water mixture.

The recovery of the used catalysts

When the oxidation reaction was finished, the flask was cooled down to room temperature and the heterogeneous catalyst Co/rGO was recycled from the reaction mixture by filtration and washed with ethyl acetate which was combined with the reaction filtrate for the next gas chromatograph (GC) analysis. On the other hand, the recycled Co/rGO was purified by lyophilization.

Characterization

The crystal structure was studied by X-ray diffractometer (D8 Focus, Bruker) with a Cu K α irradiation source (λ =1.54 Å). Transmission electron microscopy (TEM) image was observed by JEOL JEM-1200EX electron microscope performed at an accelerating voltage of 100 kV. X-ray photoelectron spectra (XPS) was recorded on a ThermoFisher K-Alpha System. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis was performed on a PerkinElmer 8300 analyzer. Field-emission scanning electron microscope (FE-SEM) image and energy dispersive spectroscopy (EDS) data of the sample were carried out on JSM-7001F SEM unit.

Conflicts of interest

There are no conflicts to declare.

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