Highly Efficient Hybrid Cobalt–Copper–Aluminum Layered Double Hydroxide/Graphene Nanocomposites as Catalysts for the Oxidation of Alkylaromatics

Renfeng Xie, Guoli Fan, Lan Yang, and Feng Li*^[a]

The selective oxidation of alkylaromatics is of vital importance for the production of high-added-value raw materials. The development of highly efficient heterogeneous catalytic oxidation systems under mild conditions has become an attractive research area. In this work, hybrid Co–Cu–Al layered double hydroxide/graphene (CoCuAl-LDH/graphene) nanocomposites, which were assembled successfully by a one-step coprecipitation route without the use of any additional reducing agents, were used as highly efficient catalysts for the liquid-phase selective oxidation of ethylbenzene using *tert*-butyl hydroperoxide as the oxidant. A series of characterizations revealed that graphene could stabilize CoCuAl-LDH nanoplatelets effectively in the nanocomposites, and in turn, highly dispersed CoCuAl-

Introduction

Nowadays, the selective oxidation of inexpensive alkylaromatics to high-added-value chemicals (e.g., ketones and aldehydes) is attracting more and more attention because of its importance both in academic research and in a variety of industrial and fine chemical processes.^[1-3] For instance, acetophenone (AP), which is commonly produced by the selective oxidation of ethylbenzene (EB), is an important intermediate for the production of esters, alcohols, aldehydes, pharmaceuticals, and resins. From both economic and environmental viewpoints, efficient and environmentally benign heterogeneous oxidation processes have become an attractive research area.^[4,5] Over the past decade, considerable endeavors have been focused on the development of non-noble-metal heterogeneous catalysts that contain earth-abundant elements. These catalysts are cost effective and tolerant to deactivation in the oxidation of alkylaromatics. For the oxidation of EB to produce AP, many heterogeneous catalysts, such as supported metal complexes,^[6-14] Mn-MCM-41,^[15,16] Co-HMS,^[17] M-APO-11 (M=Co, V, and Mn),^[18] and CeAPO-5 molecular sieves,^[19] have been explored in recent years. Although several catalysts

[a]	Dr. R. Xie, Dr. G. Fan, Prof. L. Yang, Prof. F. Li
	State Key Laboratory of Chemical Resource Engineering
	Beijing University of Chemical Technology
	P. O. BOX 98, Beijing, 100029 (P.R. China)
	Fax: (+ 86) 10-64425385
	E-mail: lifeng@mail.buct.edu.cn

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LDH could prevent the aggregation of the graphene nanosheets. By fine-tuning the mass ratio of graphene to CoCuAl-LDH, such nanocomposites offered a tunable catalytic oxidation performance. In particular, the nanocomposite with the graphene/CoCuAl-LDH mass ratio of 0.4:1 exhibited a remarkable catalytic performance with a considerable conversion (96.8%) and selectivity to acetophenone (>95.0%), which was mainly attributed to the synergism between the active CoCuAl-LDH component and the graphene matrix in the unique hetero-nanostructure. Moreover, the as-assembled nanocomposite catalysts displayed good recyclability and were active for the selective oxidation of other alkylaromatics.

showed a good catalytic activity, a high selectivity to AP and a good stability are not easy to achieve.

Layered double hydroxides (LDHs) with the formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_{2}][A^{n-}]_{x/n} \cdot m H_{2}O$ are a class of 2D anionic clay materials.^[20] In LDHs, divalent (e.g., Mg²⁺, Ni²⁺, Zn²⁺, Cu²⁺, Co²⁺, Fe²⁺) and trivalent (e.g., AI^{3+} , Fe³⁺, Cr^{3+} , Ga^{3+} , Mn^{3+}) metal cations prearrange in order in the layer lattices at the atomic level. Recently, these low-cost materials have attracted tremendous attention because they can be used widely as catalyst precursors, catalysts, and supports.^[21] For example, Mn- or Cu-containing LDHs were found to be effective for the oxidation of EB to AP.^[22-25] In most cases, LDHs only showed moderate catalytic activity. In addition, calcined Cr-containing LDHs were active for the oxidation of EB.^[26] However, the high toxicity of Cr⁶⁺ poses serious risks to humans and the environment. More recently, our group reported Co-containing mixed metal oxides derived from LDH precursors that exhibited a good catalvtic performance in the oxidation of EB with a conversion of \approx 69% and an AP selectivity of \approx 80%.^[27] Therefore, the further improvement of the catalytic performance of LDHs-based catalysts remains a challenging task.

As the newest carbon nanomaterial, graphene with a 2D honeycomb sp² carbon lattice possesses fascinating physiochemical properties, which make it an excellent candidate for the construction of high-performance graphene-based composite nanomaterials.^[28-30] As a catalyst support, graphene displays a variety of new functionalities in photocatalysis^[31-34] and electrocatalysis^[35-38] thanks to its large specific surface area, excellent conductivity for electron capture and transport, and

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electron interaction with catalytically active particles.^[39] Over the past five years, graphene-based nanocomposites that contain metal nanoparticles and metal oxides have stimulated more and more interest^[40–45] because of the potential synergy between the components and superior functionalities for various applications as catalysts,^[46,47] electrodes,^[48,49] sensors,^[50,51] and so forth. Particularly, the dispersion of Ni- and Cr-containing LDH nanoparticles on graphene sheets can potentially provide a new way to develop dispersion-enhanced photocatalysts and electrode materials.^[52–54]

Herein, with the continuous aim to develop new, highly efficient catalysts for the selective oxidation of alkylaromatics, hybrid nanocomposites of CoCuAl-LDH and graphene, which were constructed directly through a simple one-step coprecipitation route without the use of any additional reducing agents, were explored as catalysts in the liquid-phase selective oxidation of EB to AP with *tert*-butyl hydroperoxide (TBHP) as the oxidant because of their unique nanostructures and especially because of the high dispersion of the active CoCuAl-LDH component on the graphene sheets and strong interaction between them. The as-assembled hybrid CoCuAl-LDH/graphene nanocomposites exhibited a significantly enhanced activity and selectivity to AP. Moreover, the relationship between the nanostructure of the nanocomposites and their catalytic performance was investigated.

Results and Discussion

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Characterization of graphene-based nanocomposites

The XRD patterns of pure graphene oxide (GO) and CoCuAl-LDH/graphene nanocomposites are shown in Figure 1. The



Figure 1. XRD patterns of a) LDH/G-0.8, b) LDH/G-0.6, c) LDH/G-0.4, d) LDH/G-0.3, e) LDH/G-0.2, and f) CoCuAl-LDH. The inset shows the XRD pattern of pure GO.

XRD pattern of GO shows an intense (001) peak at $2\theta \approx 10.5^{\circ}$, which indicates the oxidation of graphite that involves the introduction of O-containing functional groups between the layers of graphite.^[55,56] The XRD patterns of the CoCuAl-LDH/ graphene nanocomposites show the (003), (006), (012), (110),

and (113) diffractions of LDH materials. No (001) plane of GO can be observed, which suggests the effective conversion of GO to graphene in the final CoCuAl-LDH/graphene nanocomposites.

Raman spectroscopy was used to evaluate the graphitic microstructure of the samples. LDH/G-0.4 presents two main Raman peaks (referred to as G and D bands) at $\tilde{\nu} = 1596$ and 1350 cm⁻¹ (Figure 2), which correspond to the ordered graphit-



Figure 2. Raman spectra of LDH/G-0.4 and GO.

ic lattice vibration mode with E_{2q} symmetry and the breathing mode of K-point phonons of A_{1g} symmetry for disordered graphite, respectively.^[57] In the case of GO, the Raman peak of the G band appears at a lower wavenumber of 1580 cm⁻¹, suggestive of the conversion of graphite to graphene.^[58] Notably, the intensity ratio value of the D to G bands (I_D/I_G) increases slightly from 0.98 for GO to 1.04 for LDH/G-0.4 because of the reduction of GO that results in restored domains of conjugated carbon atoms with more structural defects.^[59] Furthermore, FTIR spectra confirm the reduction of GO and the formation of CoCuAl-LDH/graphene nanocomposites (Figure S1). Notably, for LDH/G-0.4, no adsorption bands ascribed to the C=O and C–O vibrations ($\nu_{\text{C=O}}$ and $\nu_{\text{C-O}}\text{, respectively})$ are observed at $\tilde{\nu} =$ 1724 and 1421 cm⁻¹,^[60] which indicates the removal of most of the O-containing functional groups from GO. These results demonstrate the successful assembly and hybridization of CoCuAl-LDH with graphene by a facile coprecipitation route.

We also investigated the morphology and microstructure of CoCuAl-LDH/graphene nanocomposites by SEM and TEM measurements. GO shows a typical sheetlike morphology with a wrinkle-like thin sheet and smooth surface (Figure 3). In the representative LDH/G-0.4 sample, a large number of hexagonal platelet-like LDH crystallites with a mean crystal domain of \approx 30–40 nm are decorated uniformly on the surface of transparent and flexible graphene, which reflects the good affinity between them.

Moreover, the thickness of the graphene sheets estimated by AFM (Figure S2) is in the range of \approx 0.74–1.08 nm, which is



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Figure 3. SEM and TEM images of a, c) GO and b, d) LDH/G-0.4.

consistent with the bi- and trilayer structure of graphene layers in view of the thickness of a single graphite layer (\approx 0.34 nm). Additionally, the CoCuAl-LDH nanoplatelets with an average thickness of \approx 9.0 nm are distributed over the surface of graphene. The low-temperature N₂ adsorption–desorption measurements (Figure S3) reveal noticeable hysteresis loops, which demonstrates the mesoporous nature of these nanocomposites. The BET surface areas of all nanocomposites are smaller than that of pure CoCuAl-LDH (Table S1) because of the curly structure of the graphene nanosheets in the composites.

In the course of the assembly of the CoCuAl-LDH/graphene nanocomposites, metal cations adsorbed electrostatically on the GO surface firstly precipitate to form CoCuAl-LDH nuclei, which is accompanied simultaneously by the reduction of GO to graphene in the alkali medium. Subsequently, the new CoCuAl-LDH nuclei grow gradually into larger platelet-like LDH crystals with during the aging time. Finally, CoCuAl-LDH nanoplatelets are dispersed uniformly on the graphene surface. Interestingly, the introduction of CoCuAl-LDH nanoplatelets does not change the morphology of the initial GO nanosheets. Therefore, CoCuAl-LDH nanoplatelets may play a significant role in the prevention of the restacking of the graphene sheets, and graphene in turn provides sites of negative charge to anchor the LDH nanoplatelets through electrostatic interaction, which thus inhibits the agglomeration of the LDH nanoplatelets to a certain extent and facilitates the dispersion of reaction sites.

Surface compositions and chemical states

The surface compositions and chemical states of the hybrid nanocomposites were investigated by high-angle annular darkfield scanning transmission electron microscopy (HAADF-STEM) and X-ray photoelectron spectroscopy (XPS). HAADF-STEM elucidates a high dispersion of CoCuAl-LDH nanoplatelets on the graphene surface (Figure 4a), and the elemental mapping



Figure 4. a) HAADF-STEM image of LDH/G-0.4, and element mapping images of b) C-k, c) O-k, d) Co-k, e) Cu-k, and f) Al-k in LDH/G-0.4.

images of C, O, Co, Cu, and Al in LDH/G-0.4 depict the uniform distribution of Co, Cu, and Al elements in the LDH nanoflakes (Figure 4b-f).

XPS results confirm the existence of C, O, Co, Cu, and Al without impurities in LDH/G-0.4 (Figure 5a). The C1s spectrum of GO can be deconvoluted into four peaks centered at binding energies (BEs) of 289.2, 288.0, 286.9, and 284.5 eV (Figure 5 b), which are assigned to carbon atoms in different functional groups: O-C=O, C=O, C-O in C-O-C or C-O-H, and C–C (graphite; including C–C, C=C, and C–H), respectively.^[61,62] As a comparison, LDH/G-0.4 shows significantly reduced peak intensities of the carbon atoms associated with O-containing groups, especially epoxide and carbonyl functional groups, indicative of the deoxygenation of GO. This observation demonstrates the reduction of GO in the course of the assembly, and a small amount of O-containing groups still remain on the graphene surface. These remaining surface O-containing functional groups can provide anchoring sites for the LDH nanoplatelets and thus realize the stabilization of CoCuAl-LDH. Here, NaOH can act as both the precipitant for the formation of CoCuAl-LDH and the reactant for the deoxygenation of O-containing groups in GO.[63]

In the Co2p XPS spectrum of CoCuAl-LDH (Figure 5c), two peaks at BE = 780.5 and 785.3 eV are attributed to $Co 2p_{3/2}$ and a shake-up satellite peak for Co²⁺ species,^[64] whereas the two peaks at BE = 796.6 and 802.6 eV are assigned to $Co 2p_{1/2}$ and its satellite peak because paramagnetic Co²⁺ possesses a strong satellite peak. In the case of CoCuAl-LDH, the fine spectrum of Cu2p (Figure 5d) shows two broad peaks centered at $BE \,{\approx}\, 933.4$ and 942.2 eV, which are related to $Cu \, 2p_{_{3/2}}$ and a shake-up satellite peak for Cu²⁺ ions, respectively. Compared to those for pure CoCuAl-LDH, the BE values of Co2p and Cu2p for LDH/G-0.4 shift slightly to higher values. It is known that the BE shifts of elements are mainly associated with the change in the chemical microenvironments of the elements.^[65,66] The present positive shifts in the BEs of Cu²⁺ and Co²⁺ species in the spectra of LDH/G-0.4 imply the existence of interactions between positively charged brucite-like layers of CoCuAl-LDH crystallites and partial negatively charged O-con-





Figure 5. a) XPS survey spectrum of LDH/G-0.4, and b) C1s, c) Co2p, and d) Cu2p spectra of LDH/G-0.4 and CoCuAl-LDH.

taining groups of the graphene support because of the highly hybridized nanostructure of the CoCuAl-LDH/graphene composites. Such positive shifts of the BEs of metal elements also can be found in other graphene-based composites reported previously.^[67–69]

Selective oxidation of EB

The selective oxidation of EB was chosen as a model reaction to study the catalytic performance of hybrid CoCuAl-LDH/graphene nanocomposites, and the catalytic results using TBHP as the oxidant are summarized in Table 1. The main products of the oxidation of EB are AP, benzaldehyde (BA), and 1-phenylethanol (1-PA), and no byproducts related to oxidation of the aromatic ring are detected by GC–MS for all the reactions. In the absence of catalyst, a low EB conversion of 7.1% is obtained. Bare GO and graphene also show a low activity for the oxidation of EB (13.5 and 9.0% conversion, respectively). In contrast, pristine CoCuAl-LDH exhibits a much better catalytic performance with an EB conversion of $\approx 68.8\%$ and AP selectivity of $\approx 88.1\%$. These results imply that Co²⁺

and Cu^{2+} species in the CoCuAl-LDH are the catalytically active sites.

Notably, the catalytic activity of hybrid CoCuAl-LDH/graphene nanocomposites can be optimized by adjusting the mass ratio of graphene to CoCuAl-LDH. With the gradual introduction of graphene, the EB conversion is improved slightly in the case of LDH/G-0.2. As the graphene/LDH mass ratio further

Table 1. The results of the EB oxidation over different catalysts. ^[a]										
Entry	Catalyst	Co ^[b] [wt %]	Cu ^[b] [wt %]	Conversion [%]	S AP	electiv [%] BA	ity 1-PA	TON [mol/mol]		
1	blank	-	_	7.1	40.5	38.2	21.3	-		
2	GO	-	-	13.5	16.3	69.5	14.2	-		
3	graphene	-	-	9.0	29.0	54.3	16.7	-		
4	CoCuAl-LDH	10.9	4.8	68.8	88.1	10.3	1.6	23.2		
5	LDH/G-0.2	9.0	4.0	69.7	86.0	12.1	1.9	27.8		
6	LDH/G-0.3	8.4	3.7	92.2	94.7	3.8	1.3	43.5		
7	LDH/G-0.4	7.7	3.5	96.8	95.4	4.2	0.4	50.1		
8	LDH/G-0.6	6.9	3.1	87.8	87.7	10.7	1.6	46.9		
9	LDH/G-0.8	6.1	2.8	76.9	78.1	19.7	2.2	41.1		
10	LDH+graphene ^[c]	-	-	52.4	81.6	11.8	6.6	-		
[a] Rea	[a] Reaction conditions: EB 10 mmol; TBHP 40 mmol; catalyst 0.1 g; reaction tempera- ture 120 °C; reaction time 12 h. [b] Determined by ICP-AES. [c] CoCuAl-I DH mixed									

increases to 0.3:1, both the conversion and the selectivity to AP are improved sharply. In particular, a remarkably high EB conversion of 96.8% with a high AP selectivity of 95.4% is achieved over LDH/G-0.4. If the graphene/LDH mass ratio exceeds 0.4, the catalytic activity, however, begins to decrease rapidly, as indicated by the decreased conversion from 96.8 over LDH/G-0.4 to 76.9% over LDH/G-0.8, mainly because the excess gra-

physically with pure graphene.



phene inhibits the exposure of the active CoCuAl-LDH phase and because of the decreased amounts of total active Co²⁺ and Cu²⁺ species. Compared with LDH/G-0.4, the physical mixture of CoCuAl-LDH and graphene with the same graphene/ LDH mass ratio as that of LDH/G-0.4 shows a much lower activity. In addition, the turnover number (TON) for LDH/G-0.4 is higher than that of the other composites (Table 1). These results demonstrate strongly that the synergistic effect between the graphene matrix and the CoCuAl-LDH component in the nanocomposites plays an important role to govern the catalytic performance. In addition, the reaction of entry 7 in Table 1 was further performed in a filtered solution. After 2 h reaction, the catalyst was removed by hot filtration. Subsequently, under identical conditions, the reaction continues, and the EB conversion is increased by less than 3% after 10 h reaction. This demonstrates that the reaction takes place mostly on the heterogeneous surface of the CoCuAl-LDH/graphene nanocomposite.

For the catalytic oxidation of EB using TBHP as the oxidant, the catalytic performance of as-assembled LDH/G-0.4 is superior to that of other catalysts reported previously (Table S2),^[12,27,70-74] despite the different reaction conditions. We can see that over an excellent supported Pd^{II} nanoparticle catalyst,^[70] the EB conversion reaches 92.3 % with a high AP selectivity of 93.5 % at 130 °C for 12 h. Other Mn- and Co-containing heterogeneous catalysts only exhibit a moderate catalytic activity,^[12,71-74] and our Co-based catalyst reported previously is less active than LDH/G-0.4.^[27]

As a result, the CoCuAl-LDH/graphene nanocomposites are highly efficient to catalyze the oxidation of EB to AP in terms of both the activity and the selectivity to AP. In particular, LDH/ G-0.4 is more active than other composites. The BET surface area of LDH/G-0.4 is similar to that of the other composites, but the CoCuAl-LDH content is lower than that in LDH/G-0.2. Therefore, the amount of the CoCuAl-LDH component in the composites does not play a crucial role to achieve a high catalytic performance. The excellent catalytic efficiency could result from the following four factors: (i) the effective chemical adsorption of EB molecules on the graphene surface through π - π interactions and the close contact of EB with the adjacent active Co and Cu species in the lattice structure of LDH anchored onto the graphene are favorable for the oxidation of EB; (ii) the nature of the good dispersion and small size of the CoCuAl-LDH nanoplatelets is associated with the high catalytic performance, in spite of a little aggregation of LDH particles; (iii) the graphene support not only restricts the aggregation or migration of CoCuAl-LDH nanoplatelets but also interacts strongly with the active Co²⁺ and Cu²⁺ species to thus promote the activation of TBHP; (iv) in the selective oxidation of EB, a certain amount of water can be produced. Fortunately, the graphene nanosheets in the composites are beneficial for the adsorption of weakly polar EB because of its hydrophobic properties^[75] but not for the adsorption of polar water. This is a positive factor in the enhancement of the EB conversion. Therefore, the synergistic effect between CoCuAl-LDH and graphene in the nanocomposites can improve the catalytic performance of hybrid nanocomposites in EB oxidation greatly.

In view of these experimental results and the studies of pioneers,^[6, 15, 18, 76] a plausible mechanism for the liquid-phase oxidation of EB over as-assembled CuCoAl-LDH/graphene composites is proposed (Scheme 1). It is well known that the oxidation of EB is supposed to occur through a free radical mechanism to yield primarily the ethylbenzene hydroperoxide intermediate.^[76] Co²⁺ and Cu²⁺ species have been reported widely as efficient catalytically active sites for a variety of oxidation reactions. In this work, these active electron-deficient metal species in nanocomposites, as evidenced by the XPS results, would be favorable for the adsorption of TBHP and thus promote the activation of TBHP to form ethylbenzene hydroperoxide. Firstly, TBHP can be activated by coordination to the immobilized active Co^{2+} and Cu^{2+} species in LDHs to generate tert-butyl oxygen radicals and hydroxyl radicals.^[6] Secondly, the α -H of EB reacts with the formed radicals to yield α -ethylbenzene radicals. Subsequently, α -ethylbenzene radicals capture the hydroxyl groups of TBHP to yield 1-PA.^[15] Thirdly, the hydrogen atom of the hydroxyl group in 1-PA is captured more easily by tert-butyl oxygen radicals than the hydrogen atom in EB, and then 1-ethylbenzene oxygen radicals further capture



Scheme 1. Proposed mechanism for the oxidation of EB over the CoCuAl-LDH/graphene nanocomposite with TBHP as the oxidant.

the hydroxyl groups of fresh TBHP to yield ethylbenzene hydroperoxide.^[18] Finally, the ethylbenzene hydroperoxide intermediate may react in two different ways to form two final products, AP and BA.

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The effects of different reaction conditions on the selective oxidation of EB over the LDH/G-0.4 composite are shown in Figure 6. The reaction profile shows a rapid increase in both the EB conversion and the AP selectivity in the initial 3 h reaction period at 120 °C, and the selectivities to BA and 1-PA decrease gradually (Figure 6a). A high EB conversion of 96.8% with an AP selectivity of 95.4% is achieved at 12 h. Furthermore, if the reaction time is prolonged to 24 h, a slight reduction of the AP selectivity is observed. If the reaction temperature is elevated from 100 to 120°C, the EB conversion and AP selectivity are improved because of the increased reaction rate (Figure 6 b). If the reaction temperature is increased to 140°C, both the conversion and selectivity to AP decline. This can be attributed to a faster decomposition of TBHP and enhanced cleavage of the C–C bond at elevated temperatures. If the EB/ TBHP molar ratio is increased from 1:3 to 1:4, the EB conversion and AP selectivity increase from 85.1 and 80.6 to 96.8 and 95.4% (Figure 6 c). A further increase in the molar ratio of EB/ TBHP only leads to a slight increase in the conversion and a decrease in the selectivity. In contrast, the selectivity to AP decreases to \approx 91.7% because of the further conversion of AP to BA in the presence of excess THBP. Both the EB conversion and the AP selectivity over the LDH/G-0.4 are improved with an increased catalyst loading from 0.005 to 0.1 g (Figure 6d). A further increase in the catalyst loading from 0.1 to 0.2 g results in a slight decrease of the AP selectivity. This may be because the excess active sites are prone to adsorb AP in the presence of a higher amount of catalyst, and thus AP may be converted easily to BA.

Usually, heterogeneous nanoparticle catalysts suffer from a slightly reduced catalytic activity caused by the aggregation of nanoparticles during reactions. Consequently, the reusability of the CoCuAl-LDH/graphene composites was investigated. After the oxidation, the CoCuAl-LDH/graphene composites could be separated easily by centrifugation. LDH/G-0.4 can maintain its excellent catalytic activity without a clear loss of catalytic performance after four consecutive cycles (Figure 7). TEM of the used LDH/G-0.4 confirms that active CoCuAl-LDH



Figure 7. Recyclability of LDH/G-0.4 in the oxidation of EB. Reaction conditions: EB 10 mmol, TBHP 40 mmol, catalyst 0.1 g, reaction temperature 120 °C, reaction time 12 h.



Figure 6. Effects of the reaction parameters on the oxidation of EB over LDH/G-0.4: a) reaction time, b) reaction temperature, c) EB/TBHP molar ratio, and d) catalyst loading.

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crystals still are stabilized on the graphene surface and no clear agglomeration of LDH particles on the graphene surface occurs (Figure S4). The high stability of LDH/G-0.4 originates mainly from the strong interaction between the active LDH component and the graphene matrix.

Oxidation of other alkylaromatics and alkanes

We explored the possibility to use CoCuAl-LDH/graphene composites for the oxidation of other alkylaromatics and alkanes that contain primary, secondary, or tertiary C-H bonds under the similar reaction conditions that we used for the oxidation of EB. Toluene and cumene, which have primary or tertiary C-H bonds, can be oxidized to the corresponding aldehydes, ketones, or acids with moderate to high conversions over LDH/G-0.4 (Table 2, entries 1 and 2). LDH/G-0.4 also promotes the oxidation of alkylaromatics that contain secondary C-H bonds (1,2,3,4-tetrahydronaphthalene and diphenylmethane) with high conversions and selectivities to ketones (Table 2, entries 3 and 4). Moreover, LDH/G-0.4 is active for the oxidation of nonaromatic methylcyclohexane (Table 2, entry 5). These results indicate the wide applicability of the nanocomposites for the oxidation of alkylaromatics and nonaromatic alkanes. In future, the reaction conditions will be optimized to attain higher yields of the target products.



Conclusions

Hybrid Co-Cu-Al layered double hydroxide (CoCuAl-LDH)/graphene nanocomposites were assembled by a facile one-step coprecipitation approach. A series of characterizations revealed that small CoCuAl-LDH nanoplatelets were well dispersed on the surface of the graphene nanosheets. The as-assembled CoCuAl-LDH/graphene composite catalyst with a graphene/ CoCuAl-LDH mass ratio of 0.4:1 exhibited the best catalytic activity towards the selective oxidation of ethylbenzene with a remarkably high selectivity to acetophenone (95.4%) at 96.8% conversion. The synergy between the CoCuAl-LDH and graphene in the hetero-nanostructured composites, which could lead to the high dispersion of active Co²⁺ and Cu²⁺ species on the graphene surface and strong interactions between them, was proved to be responsible for the significantly enhanced catalytic performance. The as-assembled CoCuAl-LDH/graphene composite catalyst displayed a good recyclability and could be reused without a remarkable loss of either activity or selectivity at least four times. Such a robust CoCuAl-LDH/graphene composite with an excellent catalytic performance and high stability might become a promising candidate for potential commercial applications in the liquid-phase oxidation of alkylaromatics to produce industrially important intermediate chemicals.

Experimental Section

Assembly of CoCuAl-LDH/graphene nanocomposites

GO was synthesized from natural graphite powder by a modified Hummers method.[77] CoCuAl-LDH/graphene nanocomposites with different graphene contents were assembled directly by the coprecipitation method. Typically, Cu(NO₃)₂•9H₂O $Co(NO_3)_2 \cdot 6H_2O$ (3.75 mmol), (1.25 mmol), and Al(NO₃)₃·9H₂O (1.25 mmol) were added to deionized water (25 mL) with a certain amount of GO and then dissolved ultrasonically for 30 min. Subsequently, a base solution of NaOH (0.2 μ) and Na₂CO₃ (0.05 μ) were added dropwise into the above salt solution under vigorous stirring until the solution became pH 10.0. The resulting suspension was aged at 90°C for 6 h, and the solid was collected by filtration, washed with deionized water, and dried at $60\,^\circ\text{C}$ for 24 h in vacuum oven. The obtained products are denoted as LDH/G-x (x = 0.2, 0.3, 0.4, 0.6, 0.8), in which x is the mass ratio of graphene to LDH in the nanocomposites. For comparison, pure CoCuAl-LDH (or graphene) was synthesized without the addition of GO (or metal salts) under the above experimental conditions.

Characterization

XRD patterns of samples were collected by using a Rigaku D/Max-RB diffractometer with a graphite-filtered CuK_{α} source (λ = 0.15418 nm).



Elemental analysis was performed by using a Shimadzu ICPS-7500 inductively coupled plasma atomic emission spectrometer (ICP-AES) after the samples were dissolved in dilute HCl (6 m).

The morphology of the samples was investigated by using a fieldemission scanning electron microscope (FE-SEM, Zeiss Supra 55). TEM was performed by using a JEM-2100 Electron microscope (JEOL, Japan) operated at an accelerating voltage of 200 kV. HAADF-STEM images were recorded by using a JEOL 2010F instrument.

RT FTIR spectra were recorded by using a Vector 22 spectrometer from Bruker.

Raman spectroscopy was conducted by using a Jobin Yvon Horiba HR800 spectrometer using a 532 nm line of Ar^+ ion laser as the excitation source.

AFM was performed by using a DI nanoscope IV using a tapping mode.

Low-temperature N_2 adsorption–desorption isotherms of the samples were obtained by using a Micromeritics ASAP 2020 sorptometer apparatus at $-196\,^\circ\text{C}$. The total specific surface areas were evaluated by the multipoint BET method.

XPS was recorded by using a Thermo VG ESCALAB2201-XL X-ray photoelectron spectrometer using AlK_{α} X-rays (1486.6 eV) as the excitation source.

Catalytic tests

The oxidation reaction was performed in a glass reactor equipped with a condenser and a magnetic stirrer. Typically, substrate (10 mmol) and a certain amount of catalyst were added to a 10 mL one-necked flask, which was immersed in an oil bath, and then 70% aqueous TBHP with a certain substrate/TBHP molar ratio was added dropwise over 15 min. The reactor was heated to a certain temperature for a period of time, and the magnetic stirring speed was set at 900 rpm. After the reaction, the catalyst was separated by centrifugation, and the reaction mixture was dehydrated with anhydrous sodium sulfate. The products were analyzed quantitatively by GC (Agilent GC-7890B equipped with a DB-WAX capillary column; 30.0 m \times 320 μ m \times 0.25 μ m) with a flame ionization detector by the internal standard method using bromobenzene. All of the mass balances were above 96%. The injector temperature and detector temperature were set at 250 °C. The column temperature was increased from 100 to 120 °C with a ramp rate of 5 °C min⁻¹ and then to 200 $^\circ\text{C}$ with a ramp rate of 20 $^\circ\text{C}\,\text{min}^{-1}$ and held at 200 °C for 1 min. The products were further identified by GC-MS (Shimadzu QP 2010 with a DB-5 column). The TON was calculated based on the number of moles of AP product obtained per mole of Co and Cu. Furthermore, the leaching of the metal during the course of the reaction was verified by subjecting the filtrate to another reaction under identical conditions. To investigate the reusability of the catalysts, the catalyst was removed from the reaction mixtures, washed with ethyl alcohol and acetone, and dried at 70 °C for 12 h. Then, fresh substrate and the recovered catalyst were employed in the repeated tests.

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