



## Short communication

## Highly efficient solvent-free aerobic oxidation of ethylbenzene over hybrid Zn–Cr layered double hydroxide/carbon nanotubes nanocomposite

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## ARTICLE INFO

## Keywords:

Zn–Cr layered double hydroxide  
Carbon nanotubes  
Aerobic oxidation  
Alkylaromatics  
Supported catalysts

## ABSTRACT

A new hybrid Zn–Cr layered double hydroxide/carbon nanotubes (ZnCr-LDH/CNTs) nanocomposite was fabricated and employed as a high performing and stable catalyst for aerobic oxidation of ethylbenzene (EB) into acetophenone (AP). Small-sized ZnCr-LDH nanocrystals could be highly dispersed and tightly anchored onto acid-treated CNTs, forming strong interactions between them. As-assembled ZnCr-LDH/CNTs exhibited an excellent catalytic performance with a high acetophenone selectivity of 93.7% at EB conversion of 54.2%, as well as a turnover number of 2532 mol/mol. Such unprecedented efficiency of ZnCr-LDH/CNTs originated from both highly dispersed active Cr species and strong interactions between ZnCr-LDH nanocrystals and the CNTs matrix.

## 1. Introduction

Nowadays, efficient transformations of economical hydrocarbons into the corresponding high value-added oxygenated compounds through aerobic oxidations of  $sp^3$  C–H bonds are receiving increasing attention [1]. Specially, as an ideal intermediate, acetophenone (AP), which can be industrially produced via the oxidation of ethylbenzene (EB) using TBHP, nitric acid and halides as oxidants, has been widely used to synthesize various valuable chemicals [2, 3]. In this regard, more environmental benign, inexpensive and sustainable molecular oxygen is a desired terminal oxidant from the perspective of economical and practical production.

Over the past decade, considerable research efforts have been devoted to developing various heterogeneous non-precious metal (i.e. Cr, Co, Mn, and Mo) catalysts for liquid-phase oxidation of EB [4–12]. Especially, Cu-, Mn- and Ni-containing layered double hydroxides (LDHs), with the typical brucite-type octahedral  $[M_1^{2+}_x M_2^{3+}_x (OH)_2]$  layers [13], have been employed as effective catalysts for aerobic oxidation of hydrocarbons [14–16]. However, the catalytic efficiency of the above catalysts still is not satisfactory. Therefore, it is a great challenge to obtain high performing catalysts for the green synthesis of AP through the aerobic EB oxidation using molecular oxygen, especially under solvent-free conditions.

In this communication, we fabricated a new hybrid ZnCr-LDH/carbon nanotubes (ZnCr-LDH/CNTs) nanocomposite via in situ assembly method and used it as the catalyst for highly efficient liquid-phase solvent-free oxidation of EB using molecular oxygen. For

comparison, the reaction also was performed over other two hybrid ZnCr-LDH/graphene (ZnCr-LDH/G) and ZnCr-LDH/active carbon (ZnCr-LDH/C) composites. Meanwhile, the relationship between the composite structure and their catalytic performance was preliminarily investigated.

## 2. Experimental

## 2.1. Synthesis of samples

## 2.1.1. Modification of CNTs

Pristine multi-walled CNTs with the diameter of 20–40 nm and the length of 2–10  $\mu$ m were pre-treated by concentrated nitric acid through heating at 70 °C for 12 h.

## 2.1.2. Synthesis of ZnCr-LDH/CNTs composite

The above acid-treated CNTs (0.225 g) sample was dispersed ultrasonically into 50 ml of  $Zn(NO_3)_2 \cdot 6H_2O$  (6.75 mmol) and  $Cr(NO_3)_3 \cdot 9H_2O$  (2.25 mmol) aqueous solution for 30 min. Afterwards, a 200 ml of base solution of NaOH (14.4 mmol) and  $Na_2CO_3$  (4.5 mmol) were added drop-wise into the above salt solution until pH value reached 10.0 under vigorous stirring. Then the suspension was aged at 60 °C for 12 h and the obtained precipitate was filtered, washed by deionized water and dried at 70 °C for 12 h. For comparison, two ZnCr-LDH/G and ZnCr-LDH/C hybrid composites also were synthesized according to the same procedure as that for the synthesis of ZnCr-LDH/CNTs. In the case of ZnCr-LDH/G, graphene oxide, which was used as

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the support precursor, could be reduced into graphene [6].

## 2.2. Characterization

Powder X-ray diffraction (XRD) patterns were carried out on X-ray powder diffractometer XRD-6100 (Shimadzu) using a CuK $\alpha$  source ( $\lambda = 0.15418$  nm). Shimadzu ICPS-7500 inductively coupled plasma atomic emission spectroscope (ICP-AES) was used to analyze the contents of metals in samples. The morphology of samples was observed by a field emission scanning electron microscope (FE-SEM, Zeiss Supra 55). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were carried out on a JEM-3010 transmission electron microscopy. X-ray photoelectron spectroscopy (XPS) spectra data was collected based on a VG ESCALAB 2201 XL spectrometer with a monochromatic Al K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV). Infrared spectra (IR) were recorded on a Bruker Vector-22 spectrometer. Raman spectra were performed using Jobin Yvon Horiba HR800 spectrometer with an excitation source of Ar<sup>+</sup> ion laser at 532 nm.

## 2.3. Aerobic oxidation of EB

The solvent-free oxidation of EB was carried out in an autoclave reactor with a quartz insert inside and a magnetic stirrer, where EB (10 ml, 81.7 mmol) and the catalyst (0.1 g) were charged. First, the reactor was purged with pure oxygen flow for ten times. Subsequently, the reactant was heated to a certain reaction temperature, and then the oxygen pressure was set at 1.0 MPa. Afterwards, the reaction began by magnetic stirring at a speed of 900 rpm. Finally, reaction products were quantitatively analyzed using an Agilent GC-7890B gas chromatography equipped with a DB-WAX capillary column and a flame ionization detector using bromobenzene as the internal standard. In all cases, the carbon balances were more than 96%. Furthermore, the turnover number (TON) value was determined according to the mole number of AP obtained per mole of Cr in samples.

## 3. Results and discussion

### 3.1. Structural characterization

Fig. 1 shows the XRD patterns of different hybrid composites. Obviously, XRD patterns of all samples display intensive characteristic diffractions of (003), (006), (012), (110) and (113) planes for hydroxalite-like compounds [17]. For ZnCr-LDH/CNTs, a very weak diffraction appears at about 26°, which is indexed to the (002) plane of graphitic carbon (JCPDS No. 41-1487) [18], indicative of the presence

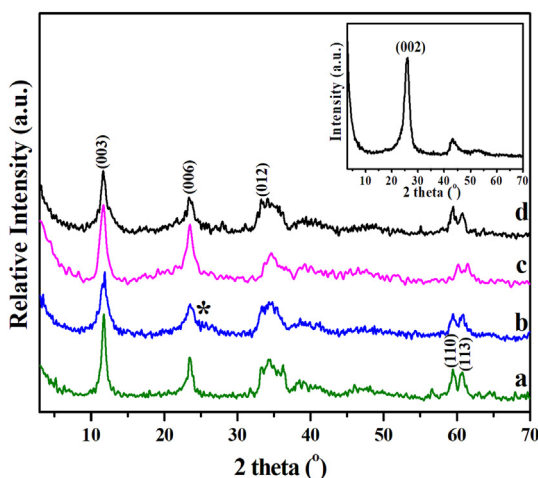


Fig. 1. XRD patterns of ZnCr-LDH (a), ZnCr-LDH/CNTs (b), ZnCr-LDH/G(c) and ZnCr-LDH/C (d) samples. The inset shows the XRD pattern of modified CNTs.

of CNTs in the sample. In two cases of ZnCr-LDH/G and ZnCr-LDH/C samples, besides those for crystalline ZnCr-LDH phase, no diffractions related to carbon materials, such as graphitic carbon, graphene or graphene oxide phases, can be detected, owing to the highly dispersed nanostructure of composites, as well as the presence of amorphous carbon.

The microstructure of ZnCr-LDH/CNTs composite was observed by HRTEM observation (Fig. 2). It is noted that small-sized and highly dispersed platelet-like ZnCr-LDH NPs with the average crystallite size of  $\sim 10$  nm attach onto the surface of CNTs with the average outer diameter of 30–50 nm, mirroring the high affinity between them and the possible formation of strong interactions between them. These small-sized ZnCr-LDH nanocrystals are beneficial to the exposure of catalytically active sites. In contrast, for ZnCr-LDH/G composite, large quantities of ZnCr-LDH particles of about 30–40 nm in size are uniformly distributed over the surface of sheet-like and wrinkle-like graphene support, as evidenced by SEM images (Fig. S1), while serious aggregation of particles composed of ZnCr-LDH and active carbon can be observed in the case of ZnCr-LDH/C sample, reflecting the mixed state between them. The above results clearly illustrate that CNTs as the support can effectively reduce the agglomeration of LDH particles to a large extent.

As can be seen in Fig. 3, the fine spectrum of Zn 2p region presents two main peaks locating at about 1022 eV–1024 eV for Zn 2p<sub>3/2</sub> core level and 1045–1047 eV for Zn 2p<sub>1/2</sub> core level, respectively, indicative of the presence of Zn<sup>2+</sup> ions [19]. And, in the fine spectrum of Cr 2p region, two strong peaks are assigned to Cr 2p<sub>3/2</sub> and Cr 2p<sub>1/2</sub> core levels at about 577–579 eV and 586 eV–589 eV, respectively, indicating that Cr species should exist in the form of Cr<sup>3+</sup> ions [20]. Interestingly, compared with those for pristine ZnCr-LDH, the binding energies (BEs) of Zn 2p and Cr 2p regions for all composites obviously shift to the higher values. Especially, ZnCr-LDH/CNTs presents the largest positive shifts in the BEs of Zn 2p and Cr 2p regions. Such significant change in the BEs of metal elements for ZnCr-LDH/CNTs is very similar to those for TiO<sub>2</sub>/CNTs, Pt/CNTs and Cu<sub>2</sub>S/CNTs composites reported in the literature [21, 22]. In our case, the shift toward higher BEs for Zn and Cr elements in ZnCr-LDH/CNTs should be associated with the highly dispersive nature of ZnCr-LDH nanocrystals and thus the formation of stronger electronic interaction between ZnCr-LDH and CNTs (i.e., charge transfer from surface ZnCr-LDH to CNTs), thereby leading to the decreased electron densities of Zn<sup>2+</sup> and Cr<sup>3+</sup> species. Moreover, Raman spectra of acid-treated CNTs and ZnCr-LDH/CNTs (Fig. S2) reveal two Raman bands at about 1347 (D-band) and 1579 cm<sup>-1</sup> (G-band), respectively, which are correlated with disordered carbon atoms and sp<sup>2</sup>-bonded carbon atoms in the hexagonal lattice [23]. Correspondingly, the significant increase in the intensity ratio of D band to G band from CNTs (0.68) to ZnCr-LDH/CNTs (0.86) demonstrates the presence of more surface structural defects of CNTs in the ZnCr-LDH/CNTs, mainly due to the strong interaction between thin ZnCr-LDH nanoplates and CNTs [24].

### 3.2. Catalytic performance of nanocomposites

The solvent-free aerobic EB oxidation was conducted over different composites using molecular oxygen as the oxidant, and the reaction results are summarized in Table 1. Herein, EB can be oxidized to produce AP, 1-phenylethanol (1-PA) and benzaldehyde (BA), and the oxidation of aromatic ring in EB does not take place. It is noteworthy that the absence of any catalyst leads to a low EB oxidation of 5.1% (Table 1, entry 1). Over acid-treated CNTs, EB conversion only reaches 7.0% (Table 1, entry 2). In contrast, pristine ZnCr-LDH possesses a better catalytic activity, along with an EB conversion of 37.9% (Table 1, entry 3), despite a lower AP selectivity of 78.5%. Notably, the catalytic performance of ZnCr-LDH/CNTs nanocomposite is significantly improved, along with both high EB conversion (54.9%) and high AP selectivity (93.7%) after 6 h (Table 1, entry 4). Compared with ZnCr-LDH/CNTs,

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