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Research paper

Insight into the preparation of Fe_3O_4 nanoparticle pillared layered double hydroxides composite via thermal decomposition and reconstruction

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ABSTRACT

As one of layered double hydroxides (LDH) based heterogeneous catalysts, transition metal oxide pillared LDH composite has attracted considerable research interests as its excellent catalytic efficiency and thermal stability. However, during the preparation especially by reconstruction techniques, abundant interlayer regions of LDH are contaminated by some unexpected anion such as LDH affinitive CO_3^{2-}, which will result in inaccessible interlayer active site. In this paper, magnetic nanoparticle Fe_3O_4 pillared LDH composite was synthesized with exchangeable NO_3^- as the main interlayer anion by decomposition and reconstruction route. The anion exchange, decomposition and reconstruction processes were comprehensively investigated. XRD, TG-DTA-MS, SEM and other methods have been employed to characterize materials. The results show that anion exchange between ferric citrate anion and LDH follows Langmuir isotherm model and pseudo-second-order model. The decomposition and oxidation of anion exchange product (LDH-$Fe(C_6H_4O_7)^-$) can be complete at 550 °C for 20 min and crystal Fe_3O_4 with nanostructure is formed between 500 and 600 °C. When calcined product (LDO-Fe_3O_4) is reconstructed by rehydration in 0.015 M HNO_3-30 wt% $NaNO_3$ mixture aqueous solution, CO_3^{2-} contamination derived from CO_2 in air can be averted and lamellar structure is successfully recovered with Fe_3O_4 and NO_3^- remaining in the interlayer gallery of LDH.

1. Introduction

With the aim of developing new classes of selective catalysts, sandwich-like structural heterogeneous catalysts with good catalytic efficiency and stability have attracted increasing attention (Sels et al., 1999; Sels et al., 2001; Liu et al., 2009; Li et al., 2014; Hunter et al., 2016), which are generally prepared by intercalation of functional molecules into interlayer gallery of lamellar structural inorganic solids such as layered double hydroxides (LDH) (Zhao et al., 2011; Mac Leod et al., 2012; Gunjakar et al., 2013). As a type of anion exchange lamellar materials, LDH are well studied and widely used in various domains due to its excellent performance on anion exchange and facile preparation (Wang and O'Hare, 2012; Nagendra et al., 2015; Yang et al., 2016). Owing to the unique supramolecular structure with the controlled chemical composition and size of interlayer gallery, LDH is an ideal inorganic matrix for the synthesis of functional molecules intercalated LDH nanocomposites with sandwich-like structure (Darder et al., 2005). After intercalation of functional molecules, usually macromolecules with relatively higher molecular diameter such as titanium tartrate (Shi et al., 2010), paratungstate (Guo et al., 2001; Liu et al., 2008) and porphyrins (Lang et al., 2007)· (Káfuňková et al., 2010), the interlayer gallery of LDH is generally expanded to corresponding size, and consequently become a microreactor which can provide enough space for the reaction between reagents and catalytic molecules.

In the field of catalytic chemistry, transition metal oxide incorporated LDH composite has also abstracted extensive research interests and investigation (Basile et al., 2002; Zou et al., 2013; He et al., 2014), since transition metal oxide species possess good catalytic function on oxidation, polymerization, photocatalysis and so on (Greiner et al., 2012). Dvininov (Dvininov et al., 2010) reported that SnO_2/MgAl-layered double hydroxide nanocomposites prepared by wet impregnation and calcination method show a good photocatalytic activity for methylene blue decolourization and the flat band potential of SnO_2 has been shifted due to the interaction with LDH, which is energetically favourable to the formation of hydroxyl radicals. However, during the preparation and application of such LDH based transition metal oxide composite, LDH only act as a supporter and active metal oxides merely load on external surface or in some holes, leaving abundant internal surface unused. If transition metal oxide can be intercalated into the interlayer gallery of LDH in a similar way to the intercalation of catalytic anions, more transition metal oxide can be embedded both on the external and internal surface, giving abundant reactive space and active sites for catalysis. Moreover, the height of interlayer gallery can be

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adjusted to specific size, which can enhance the selectivity of catalysis to some extent (Feng et al., 2015). Villegas (Villegas et al., 2003) successfully incorporated manganese oxide species (MnOx) into the interlayer of LDH host by in-situ reduction reaction. Firstly, manganese precursor MnO_4^- was introduced into the interlayer of LDH by anion exchange, and subsequently MnO_4^- was transformed into MnOx by the reduction of organic compounds (glucose, ethanol and ascorbic acid). Accompanied by intercalation of MnOx; however, the interlayer gallery region was contaminated by such organic reductants, as the organic compounds in addition to reducing MnO_4^- ions were also partly exchanging with some of the counter anions from the interlayer. Moreover, not all transition metal has its corresponding oxyacid root and can be transformed into metal oxide species by reduction.

Thermal decomposition-reconstruction method, which is a common route for the intercalation of some anions with different molecular size into LDH, can be adopted and improved to synthesize transition metal oxide pillared LDH composite. This synthetic route includes three processes: (I) anion exchange of transition metal precursor, (II) decomposition of transition metal precursor intercalated LDH to form transition metal oxide and layered double oxides composite, and (III) reconstruction of lamellar structure to obtain transition metal oxide pillared LDH. Transition metal precursor can be settled on abundant metal organic complex anions or metal oxyacid roots. Although decomposition-reconstruction method is a reasonable route, there is little report about preparation of transition metal oxide pillared LDH by this method. Gérardin (Gérardin et al., 2008) synthesized Ni^0 intercalated LDH nanocomposites by thermal reduction of Ni hydroxyl citrate species intercalated Mg_2Al layered double hydroxides in H_2 atmosphere and reconstruction of calcined oxide compounds in aqueous solution. However, the interlayer gallery of regenerated Ni^0-LDH is occupied by stable CO_3^{2-} that is unable to exchange with other anions, which means the reactant ions cannot get access to the active Ni^0 particles loaded in the interlayer space and consequently the catalytic efficiency is reduced.

During the rehydration procedure, the contamination and occupation of interlayer gallery by stable CO_3^{2-} derived from CO_2 in air has been always observed. Rocha (Rocha et al., 1999) reconstructed calcination products of Mg-Al-CO_3 LDH in saturated NH_4Cl solution. However, the d_{003}-value after reconstruction is only 7.65 Å, indicating CO_3^{2-} is the main interlayer anion in reconstructed LDH. Lv (Lv et al., 2006a; Lv et al., 2006b) adopted calcined Mg-Al-CO_3 LDH to remove fluoride and chloride ions from aqueous solution, expecting intercalation of such halogen elements. However, the height of interlayer gallery was the same as that of Mg-Al-CO_3 LDH, meaning fluoride and chloride ion did not intercalated into the interlayer as expected. Only if the solute molecular contains some functional groups which have a strong affinity with LDH such as carboxylic and sulfonic groups, the interlayer of reconstructed LDH can be partly intercalated by such special molecular with partial contamination of CO_3^{2-} (You et al., 2002; El Gaini et al., 2009). Therefore, the methods for eliminating or abating the contamination of CO_3^{2-} during the reconstruction has been an important issue, since it is significant for decomposition-reconstruction route as well as the application of transition metal oxide pillared LDH, on account of giving an accessible interlayer gallery for catalysis reaction. However, previous studies concerning about decomposition and reconstruction of LDH species mainly focus on the recovery of lamellar structure and crystal growth or adsorption performance of LDH composite material.

In this study, magnetic nanoparticle Fe_3O_4, an important catalyst in many important chemical reactions, was intercalated into the interlayer gallery of LDH with exchangeable NO_3^- as the main interlayer anion by decomposition-reconstruction route. As a typical example for preparation of transition metal oxide pillared LDH composite heterogeneous catalyst, anion exchange of ferric citrate anion (transition metal precursor), decomposition and reconstruction process were comprehensively studied, providing an insight into the synthesis process. Thermodynamics and kinetics of anion exchange process was discussed. Thereafter, the crystal structure variation of calcined LDH, as well as the gas generated during decomposition were both analysed. Most importantly, the variation of interlayer anion during reconstruction in different solutions, as well as the kinetics property of reconstruction were also investigated in detail.

2. Experimental section

2.1. Materials

Reagents used in this study were analytical grade and purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. including zinc chloride ($ZnCl_2$), aluminium chloride crystal ($AlCl_3 \cdot 6H_2O$), sodium hydroxide (NaOH), nitric acid (HNO_3), sodium nitrate ($NaNO_3$) and catechol ($C_6H_6O_2$) and glycine ($C_2H_5NO_2$). Ammonium ferric citrate was purchased from Aladdin Industrial Corporation and its Fe content was 21.6% as determined by ICP-OES; therefore, its molecular formula was proposed as $NH_4Fe(C_6H_4O_7)$.

2.2. Synthetic method

LDH were prepared by a facile method which involves a rapid mixing and nucleation process, followed by a separate aging process (Zhao et al., 2002). Solution A: $ZnCl_2$ and $AlCl_3 \cdot 6H_2O$ with Zn^{2+}/Al^{3+} ratios of 2.0 were dissolved in deionized water (100 mL) to give solutions with an Zn^{2+} concentration of 0.6 M. Solution B: NaOH were dissolved in decarbonated water (100 mL) with an concentration of 1.8 M. The concentration of NaOH correlated with the concentration of metal and calculated according to the stoichiometric LDH molecular formula ($Zn_2Al(OH)_6Cl \cdot 2H_2O$): $C_{NaOH} = (C_{Zn} + C_{Al}) \times 2$. Two solutions were simultaneously added into a flat-bottomed flask which contained 300 mL decarbonated water in advance and mixed at 1000 rpm for 30 min under N_2 atmosphere to prevent CO_2 contamination. The solid-to-liquid ratios (S/L) defined as the proportion of stoichiometric mass of LDH solid (g) to the volume of the reaction liquid (mL) were set as 1/25, 1/50 and 1/100. The flask with resulting suspension was sealed and aged at 80 °C for 12 h. The final precipitate was separated by centrifugation and extensively washed with decarbonated water. The wet LDH were divided in two portions: one was vacuum freeze drying for analysis, and the another part was used in the followed synthesis. The decarbonated water was produced by boiling deionized water at 100 °C for 10 min and the LDH was denominated as Zn_2Al-Cl.

Iron oxide pillared LDH were prepared firstly by anion exchange between ammonium ferric citrate and LDH. The ammonium ferric citrate solutions of different concentrations were added into the LDH suspension to reach a final S/L ratio of 1/50 and the suspension was stirred at 500 rpm. The adsorption isotherms and kinetics were investigated based on the equilibrium concentrations of Fe in filtrate. After centrifugation and vacuum freeze drying, the exchange product designated as LDH-$Fe(C_6H_4O_7)^-$ was then subjected to thermal analysis by TG-DTA-MS and decomposition at different temperature in order to obtain its oxide forms. The oxide compound derived from decomposition of LDH is denominated as LDO. Finally, this oxide compound designated as LDO-Fe_3O_4 was rehydrated in HNO_3-$NaNO_3$ mixed solution with different concentrations of HNO_3 and 30 wt% of $NaNO_3$. The final yellow product (Fe_3O_4 pillared LDH with NO_3^- as the interlayer anion, designated as LDH-Fe_3O_4-NO_3) was centrifuged, washed with decarbonated water, and vacuum freeze drying prior to characterization.

2.3. Characterization techniques

The concentration of Fe was analysed by using ICP-OES (PE OPTIMA8000, PerkinElmer, Inc. America). Thermal analyses of the materials were performed in corundum crucible by thermogravimetric analysis (TG) using thermal analyses instruments (STA449F3, NETZSCH-Gerätebau GmbH, German), with air under a flow rate of 100 $cm^3\ min^{-1}$ by heating up to 1000 °C at heating rate of 10 °C