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Short communication

An intracrystalline catalytic esterification reaction between ethylene glycol intercalated layered double hydroxide and cyclohexanecarboxylic acid

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ABSTRACT

An intracrystalline catalytic esterification between ethylene glycol intercalated NiAl layered double hydroxide and cyclohexanecarboxylic acid is developed. It leads to much higher deacidification efficiency than the bulk catalytic reaction. The intracrystalline catalytic reaction mechanism has been proposed.

1. Introduction

LDHs are a class of anionic layered materials that can be represented by $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot yH_2O$ [1]. Because of the layered structure and interlayer exchangeable anions, LDHs can be used as "molecular container" for immobilization of anions. It allows intracrystalline reactions in which the control of the reactant diffusion imposed by the structural nature of LDHs could strongly determine the rate [2], selectivity [3] and yield [4]. A common intracrystalline reaction is formed by intercalating one reactant into the interlayer of LDHs. Prévot et al. [4] found the O-alkylation of benzoate intercalated LDHs with alkyl halide increased ester yield and decreased by-products. Another intracrystalline reaction is formed by intercalating catalytic sites into the interlayer of LDHs [3]. Shi et al. [5] prepared titanium tartrate complex intercalated LDH as catalyst to enhance asymmetric induction in sulfoxidation of pro-chiral methyl phenyl sulfide through the constrained complex in the interlayer. However, less attention has been paid on establishing an interlayer catalytic reaction by virtue of the catalytic effect of metal sheets.

Due to the acidity or basicity of sheets, LDHs can act as esterification catalysts [6]. In a previous study [7], LDHs were used as catalysts to remove naphthenic acids from crude oil via esterification, however, this reaction suffers from diffuse limitation caused by highly viscous ethylene glycol (EG), leading to low catalytic efficiency. A possible pathway to eliminate the diffusion limitation is that EG anions are pre-immobilized in the interlayer of LDHs and then naphthenic acids diffuse into the interlayer and react with EG under the catalysis of metal ions in sheets. To date, there is no report on this intracrystalline catalytic esterification.

In this work, firstly, an EG intercalated NiAl LDH (NiAl-EG) with a Ni/Al ratio of 2 was synthesized by using nitrate LDH (NiAl–NO_3) as precursor and EG as solvent; KOH was added into EG to facilitate the deprotonation of EG. Secondly, the intracrystalline catalytic esterification of NiAl-EG with cyclohexanecarboxylic acid (Cyc) was performed and compared with the conventional bulk catalytic reaction. Herein, the Cyc in dodecane was used for the purpose of convenient analysis.

2. Results and discussion

The XRD patterns of NiAl–NO_3 and NiAl-EG are shown in Fig. 1. Each sample shows the general features of LDHs [1]. The (003) reflection of NiAl-EG shifts to a lower angle compared with that of NiAl–NO_3. The basal spacing of (003) reflection (d_{003}) is 1.12 nm, subtracting the thickness of brucite layer (0.48 nm [1]), the gallery height is 0.64 nm, larger than the length of EG (0.42 nm). Therefore, EG anions may be accommodated in the interlayer as a tilted bilayer with the negative ethyleneoxy groups attaching to the upper or lower hydroxide layers [8].

The FT-IR spectra of NiAl–NO_3, NiAl-EG and pristine EG are shown in Fig. 2A. For NiAl–NO_3, an apparent band at 1384 cm^{-1} is assigned to the $v3$ vibration of NO_3^- [1]. For NiAl-EG, there are two absorption bands at 2940 and 2880 cm^{-1} assigned to asymmetric and symmetric stretching vibrations of $-CH_2$, respectively, and two bands at 1086 and 1047 cm^{-1} ascribed to the in-plane bending vibration of $C-C-O$ [9]. Moreover, rocking vibrations of $-CH_2$ centered at 880 and 863 cm^{-1} are observed.

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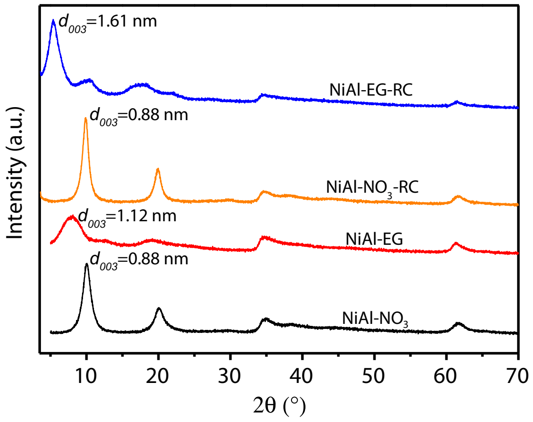

Fig. 1. XRD patterns of NiAl–NO_3, NiAl-EG, NiAl–NO_3-RC and NiAl-EG-RC.

The presence of these bands confirms EG anions within the interlayer. The band at 1383 cm^{-1} in NiAl-EG is very close to that assigned to NO_3^-, but no nitrogen is detected by elemental analysis (Table S1). Therefore, this band is ascribed to the scissoring, wagging or twisting vibration of $-CH_2$ [10]. The O–H stretching at 3367 cm^{-1} in pristine EG shifts to 3415 cm^{-1} in NiAl-EG, due to the interaction between ionized guests and layers of LDHs [11]. Additionally, owing to this interaction, the absorption bands of C–C–O of NiAl-EG shift to a higher wavenumber than those of EG [12].

The DSC curves of NiAl-EG (Fig. S1b) show a sharp and intensive exothermal peak, resulting from the decomposition and combustion of organic species in the interlayer. Moreover, the temperature of this peak (265 °C) is higher than EG's boiling point (198 °C), indicating the host–guest interaction.

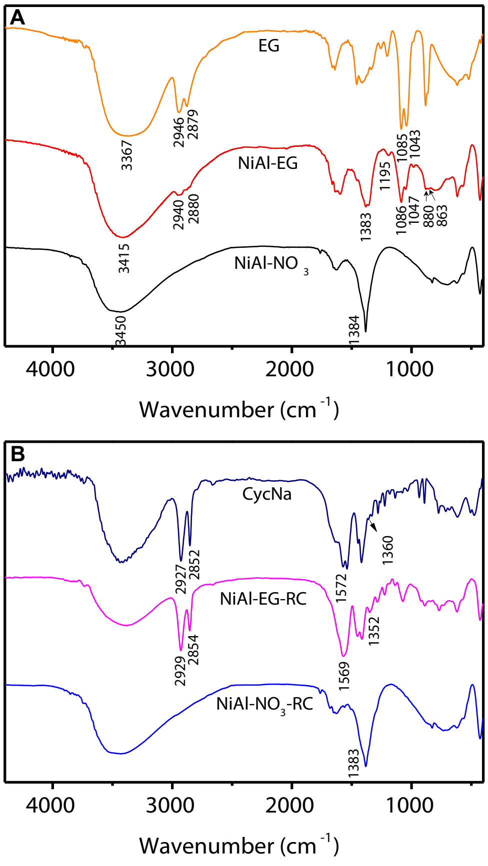

Fig. 2. FT-IR spectra of (A) NiAl–NO_3, NiAl-EG and EG; (B) NiAl–NO_3-RC and NiAl-EG-RC.

The above characterization results clearly demonstrate the successful intercalation of EG into the interlayer. According to the elemental analysis data (Table S1), the stoichiometric formula of NiAl-EG is expressed as $[Ni_{0.67}Al_{0.34}(OH)_2(C_2H_5O_2^-)_{0.33}\cdot0.32H_2O]$.

The intracrystalline catalytic esterification reaction was carried out by adding NiAl-EG (0.9 mmol EG within the interlayer) to a solution of Cyc (2.5 mmol) and dodecane. A bulk catalytic reaction over NiAl–NO_3 catalyst and a non-catalytic reaction between EG and Cyc were also performed under the same conditions, wherein the amounts of EG, Cyc and dodecane were as same as those in the intracrystalline reaction (see details in supplementary data). After reaction, NiAl-EG and NiAl–NO_3 were recovered (see details in supplementary data) and noted as NiAl-EG-RC and NiAl–NO_3-RC, respectively. The acid concentration of the solution was analyzed by GC–MS. The reaction results of the intracrystalline, bulk and non-catalytic reactions are listed in Table 1. The deacidification ratio of the intracrystalline catalytic reaction is extremely higher than that of the bulk catalytic and non-catalytic reactions.

The XRD patterns of LDHs after reaction are displayed in Fig. 1. In each case, the layer structure is remained. NiAl-EG-RC shows a d_{003} of 1.61 nm and gallery height of 1.13 nm that is almost twice the molecular size of Cyc (0.62 nm). Therefore, Cyc anions in NiAl-EG-RC may be a tilted bilayer arrangement. The XRD patterns of NiAl–NO_3 and NiAl–NO_3-RC show no obvious differences.

The FT-IR spectra of LDHs after reaction are shown in Fig. 2B. Sodium cyclohexanecarboxylate (CycNa) was used as reference. The absorption bands of $-CH_2$ in NiAl-EG-RC at 2929 and 2854 cm^{-1} are very close to those in CycNa (2927 and 2852 cm^{-1}). Additionally, two bands at 1569 and 1352 cm^{-1} in NiAl-EG-RC are corresponding to the asymmetric and symmetric vibrations of C=O in $-COO^-$ [3], respectively, suggesting Cyc anions in the interlayer. The DSC curve of NiAl-EG-RC (Fig. S2b) shows a strong exothermal peak with a maximum value at 343 °C, due to the decomposition and combustion of Cyc anions in the interlayer. These characterization results confirm the presence of Cyc anions in the interlayer of NiAl-EG-RC. According to the elemental analysis result (Table S1), the formula of NiAl-EG-RC is expressed as $[Ni_{0.68}Al_{0.34}(OH)_2(C_7H_{11}O_2^-)_{0.33}\cdot0.23H_2O]$. NiAl–$NO_3$-RC and NiAl–$NO_3$ display the similar absorption bands, indicating no changes after bulk reaction, which agrees with the TG-DSC result (Figs. S1a and S2a).

Both the unchanged NiAl–NO_3 after bulk catalytic reaction and the higher deacidification ratio than the non-catalytic reaction demonstrate the catalytic effect of LDH. By GC–MS, the ester was detected in the liquid product of intracrystalline and bulk catalytic reactions. To determine the detailed structure of this unusual ester, it was extracted from a liquid product (see details in supplementary data) and further characterized by FT-IR (Fig. S3), ^1H NMR (Fig. S4a) and ^{13}C NMR (Fig. S4b). All the results demonstrate that the esterification of EG with Cyc mainly produces 2-hydroxyethyl cyclohexanecarboxylate (CAS No. 16179-44-5).

For NiAl-EG, the Cyc in feed are removed through two paths. The first one, Cyc molecules enter the gallery of LDH and react with pre-intercalated EG under the catalysis of metal in sheets. Hence they are converted into uncharged esters which diffuse to the solution. It is proved that esters were only detected in solution and no band at

Table 1
The results of intracrystalline catalytic, bulk catalytic and non-catalytic reactions.

	Intracrystalline catalytic reaction	Bulk catalytic reaction	Non-catalytic reaction
Deacidification ratio	69.80%	2.33%	0
Ester yield	36.52%	2.33%	–
EG conversion	91.09%	7.22%	–