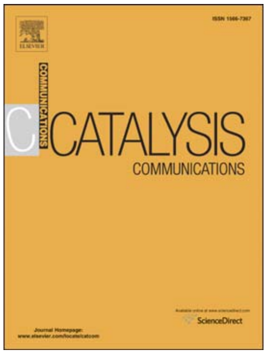


An intracrystalline catalytic esterification reaction between ethylene glycol intercalated layered double hydroxide and cyclohexanecarboxylic acid

Hao Wang, Weizhuo Duan, Yanqing Lei, Yan Wu, Ke Guo, Xiaodong Wang

PII: S1566-7367(15)00012-6
DOI: doi: 10.1016/j.catcom.2015.01.004
Reference: CATCOM 4186

To appear in: *Catalysis Communications*

Received date: 15 October 2014
Revised date: 9 December 2014
Accepted date: 6 January 2015

Please cite this article as: Hao Wang, Weizhuo Duan, Yanqing Lei, Yan Wu, Ke Guo, Xiaodong Wang, An intracrystalline catalytic esterification reaction between ethylene glycol intercalated layered double hydroxide and cyclohexanecarboxylic acid, *Catalysis Communications* (2015), doi: 10.1016/j.catcom.2015.01.004

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

Hao Wang, Weizhuo Duan, Yanqing Lei, Yan Wu, Ke Guo and Xiaodong Wang*

School of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu
610500, P. R. China

*Tel: +86-28-83037338; E-mail: swpuwh@gmail.com

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.

Keywords: Intracrystalline catalytic esterification, layered double hydroxide, deacidification

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 reactants 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 sulphide 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[7]. In pervious study[8], 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, 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[9].

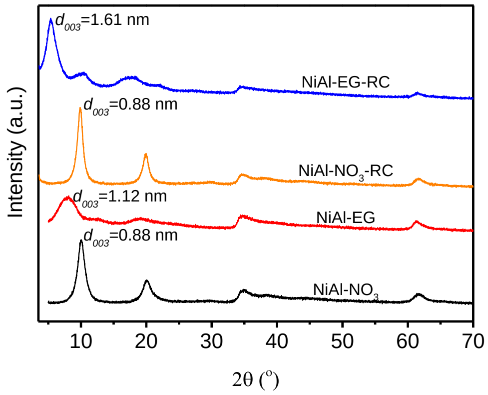


Fig. 1. XRD patterns of NiAl-NO_3, NiAl-EG, NiAl-NO_3-RC and NiAl-EG-RC

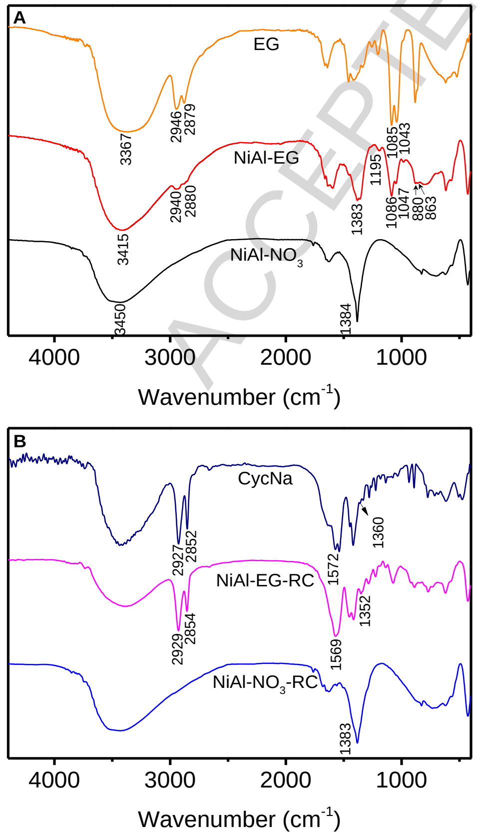


Fig. 2. FT-IR spectra of (A) NiAl-NO_3, NiAl-EG and EG; (B) NiAl-NO_3-RC and NiAl-EG-RC

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[10]. Moreover, rocking vibrations of -CH_2 centered at 880 and 863 cm^{-1} are observed. The presence of these bands confirm 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[11]. 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[12]. Additionally, owing to this interaction, the absorption bands of C-C-O of NiAl-EG shift to higher wavenumber than those of EG[13].

The DSC curves of NiAl-EG (Fig. S1b†) shows 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.

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 $[Ni_{0.67}Al_{0.34}(OH)_2(C_2H_5O_2^-)_{0.33}\cdot 0.32H_2O]$.

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 solution was analysed 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.

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%	-

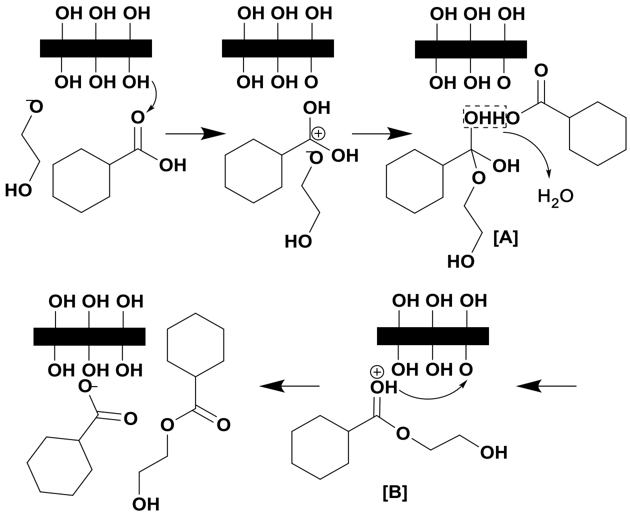
EG conversion	91.09%	7.22%	-

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 of 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 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 $[Ni_{0.68}Al_{0.34}(OH)_2(C_7H_{11}O_2^-)_{0.33}\cdot 0.23H_2O]$. NiAl-$NO_3$-RC and NiAl-$NO_3$ display the similar absorption bands, indicating no changes after bulk reaction, which agrees with TG-DSC result (Fig. S1a† and Fig. 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, 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 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 by that esters were only detected in solution and no band at 1733 cm^{-1} assigned to $v_{C=O}$ of ester (Fig. S3†) was observed in FT-IR spectrum of NiAl-EG-RC. The second one, after the consumption of EG, Cyc anions occupy the interlayer and Cyc intercalated LDH is formed. The Cyc removal ratios of the two paths can be calculated by the formula of NiAl-EG-RC and deacidification ratio, which are 36.52% (Table 1) for the first path and 33.28% for the second. It means that the deacidification ratio through esterification path or ester yield of the intracrystalline reaction is 14 times as large as that of bulk reaction. In other words, 91.09% EG (Table 1) in the interlayer was converted into ester while only 7.22% EG (Table 1) in the bulk catalytic reaction was converted, despite of the same amount of EG in both reactions. The remarkably enhanced esterification reactivity for NiAl-EG could be attributed to the following reasons. First, EG anions are confined in the nano-sized interlayer space of LDH, greatly limiting the freedom of EG and hence enhancing the collision probability between EG and Cyc. Wang *et al.*[2] also attributed the faster reaction rate of intracrystalline oxidation between thiosulfate intercalated ZnAl LDH and hexacyanoferrate (III) than that of bulk reaction to the same reason. Second, EG anions in the interlayer have higher nucleophilicity than EG molecules in liquid, favourable to attacking the less electrophilic carbon in carbonyl of Cyc. An *et al.*[3] found the proline anions intercalated in LDH were more nucleophilic than nonionized proline and thus attacked the acetone more readily, resulting in the easier formation of carbinol amine intermediate and much faster asymmetric aldol reaction rate. Third, the pre-immobilization of EG in LDH can eliminate the diffusion limitation from highly viscous EG and enlarge the interlayer space to facilitate the Cyc molecules diffusing into the interlayer.



Scheme 1 A potential mechanism of intracrystalline catalytic esterification in NiAl-EG

A potential mechanism of this intracrystalline catalytic esterification is proposed, as shown in Scheme 1.

First, due to the relatively high electronegativity of Ni, hydroxyl groups in the sheets show acidity[14] and thus the proton of hydroxyl could combine with carbonyl oxygen in Cyc to increase the electrophilicity of carbon in carbonyl. Lei *et al.*[15] also suggested that the weak acid sites on LDH sheets could interact with the carbonyl group of acetone to polarize the C=O bond and hence increase the density of positive charge on the carbon of carbonyl group. Moreover, due to the electron donation effect of guest organic anions, the O-H bonds of hydroxyls in the sheets are weakened and protons are readily produced, which enhances the acidity of layer[16]. To verify the catalytic effect of acidity, EG intercalated

MgAl LDH was synthesized and used as esterification catalyst under the same reaction conditions. Its deacidification ratio is 52.32% and lower than that of NiAl-EG (69.80%), indicating that more acidic NiAl sheets show better catalytic effect.

Second, the carbonyl carbon with increased electrophilicity is then attacked by EG anions with enhanced nucleophilicity in the interlayer and an intermediate [A] is produced. Li *et al.*[7] reported that the deprotonated EG helps to the esterification between EG and naphthenic acid in vacuum gas oil.

Third, [A] is converted into another intermediate [B] through the loss of water from the hydroxyl of [A] and proton of Cyc. Dodecane is an apolar aprotic solvent, in which Cyc could not ionize. Therefore, Cyc anions should be generated from the intracrystalline esterification.

Fourth, [B] may lose proton to compensate the sheets and form ester product accompanying with the recycle of catalyst. The similar recycle of H^+ from LDH sheets was also reported by Lei *et al.*[7].

Finally, Cyc anions enter the interlayer of LDH as counter ions, and ester products diffuse to the solution.

To confirm the intracrystalline reaction, a reaction with equimolar amount of EG (in the interlayer of NiAl-EG) and Cyc was performed. Ester product was detected in the solution, whereas EG was not detected. It suggests the esterification occurs in the interlayer instead of in the solution through the exchange between Cyc and EG.

The FT-IR and XRD characterization results for LDH collected with different reaction time are given in Fig. S5†, S6† and Table S2†. It is found that Cyc and EG could co-exist in the interlayer of LDH when the reaction time is short, due to the rapid reaction and consumption of EG. Moreover, the concentration of Cyc in liquid at different reaction time is shown in Fig. S7†. It declines sharply before 20 min due to the quick diffusion and reaction of Cyc in the interlayer. Chen *et al.*[17] and Wang *et al.*[2] also found the similar result during the intracrystalline oxidation reactions in LDH. It is worth noting that no EG was detected by GC-MS in the solution at different reaction time, which proves that EG may react with Cyc in the interlayer rather than in solution.

According to the above mechanism and analysis results, the steps of this intracrystalline catalytic esterification could be proposed (Scheme S1†): (1) Cyc molecules transfer from the bulk solution to the edge of NiAl-EG; (2) Cyc molecules diffuse into the interlayer; (3) the esterification occurs between Cyc and pre-intercalated EG anions in the interlayer under the catalysis of metal in sheets; (4) the uncharged esters diffuse to the edge of LDH; (5) the esters enter solution, leaving Cyc anions in the interlayer.

NiAl-EG-RC can be regenerated into NiAl-EG by treatment with the solution containing KOH and EG, and the deacidification ratio can be maintained. Prévot *et al.*[4] also regenerated the bromide intercalated LDH produced by the intracrystalline reaction into benzoate intercalated LDH through re-exchanging with benzoate solution.

3. Conclusion

The intracrystalline catalytic esterification between NiAl-EG and Cyc has been developed. NiAl-EG is synthesized via ion exchange under mild conditions by the aid of KOH. The immobilized EG in LDH can react with the Cyc diffusing into the interlayer and produce ester entering liquid. Cyc anions occupy the interlayer after EG anions are consumed. Deacidification ratio, ester yield and EG conversion of intracrystalline reaction reach up to 69.80%, 36.52% and 91.09%, respectively, extremely higher than those of the bulk catalytic reaction over NiAl-NO_3 (2.33%, 2.33% and 7.22%). The confined interlayer enhances the collision probability between EG anions and Cyc. EG anions pre-intercalated in LDH display increased nucleophilicity and eliminate the diffusion limitation, moreover, the enlarged interlayer space facilitates Cyc diffusing into the interlayer.

■ Acknowledgments

The authors acknowledge the financial support from the National Natural Science Foundation of China (20906075) and the Foundation of State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation (PLN1127).

■ References

[1] F. Cavani, F. Trifirò, A. Vaccari, Hydrotalcite-type anionic clays: preparation, properties and applications, Catal. Today 11 (1991) 173-301.

[2] L.G. Wang, T. Yuan, Y. Li, W. Shi, Z.M. Ni, Interlayer reaction of thiosulfate in a confined region of layered double hydroxides, Acta Phys. -Chim. Sin. 28 (2012) 273-282.

[3] Z. An, W. Zhang, H. Shi, J. He, An effective heterogeneous L-proline catalyst for the asymmetric aldol reaction using anionic clays as intercalated support, J. Catal. 241 (2006) 319-327.

[4] V. Prévot, B. Casal, E. Ruiz-Hitzky, Intracrystalline alkylation of benzoate ions into layered double hydroxides, J. Mater. Chem. 11 (2001) 554-560.

[5] H. Shi, C. Yu, J. He, Constraining titanium tartrate in the interlayer space of layered double hydroxides induces enantioselectivity, J. Catal. 271 (2010) 79-87.

[6] F. Hamerski, M.L. Corazza, LDH-catalyzed esterification of lauric acid with glycerol in solvent-free system, Appl. Catal. A-Gen. 475 (2014) 242-248.

[7] X. Li, J. Zhu, Q. Liu, B. Wu, The removal of naphthenic acids from dewaxed VGO via esterification catalyzed by Mg–Al hydrotalcite, Fuel Process. Technol. 111 (2013) 68-77.

[8] Y. Wu, H. Wang, T. Zhong, L. Zhang, L.J. Xu, Characterization of mgal hydrotalcites prepared by various methods and their catalytic activities for esterification to remove acid from crude oil, Acta Petrolei Sinica(Petroleum Processing Section) 27 (2011) 687-693.

[9] S. Gago, T. Costa, J.S. de Melo, I.S. Gonçalves, M. Pillinger, Preparation and photophysical

characterisation of Zn–Al layered double hydroxides intercalated by anionic pyrene derivatives, J. Mater. Chem. 18 (2008) 894-904.

[10] J.L. Guimarães, R. Marangoni, L.P. Ramos, F. Wypych, Covalent grafting of ethylene glycol into the Zn-Al-CO_3 layered double hydroxide, J. Colloid Interface Sci. 227 (2000) 445-451.

[11] K. Fukushima, H. Matsuura, Infrared spectroscopic study of solid films of poly(ethylene glycol) doped with cations, J. Mol. Struct. 350 (1995) 215-219.

[12] V. Prévot, C. Forano, J.P. Besse, F. Abraham, Syntheses and thermal and chemical behaviors of tartrate and succinate intercalated Zn_3Al and Zn_2Cr layered double hydroxides, Inorg. Chem. 37 (1998) 4293-4301.

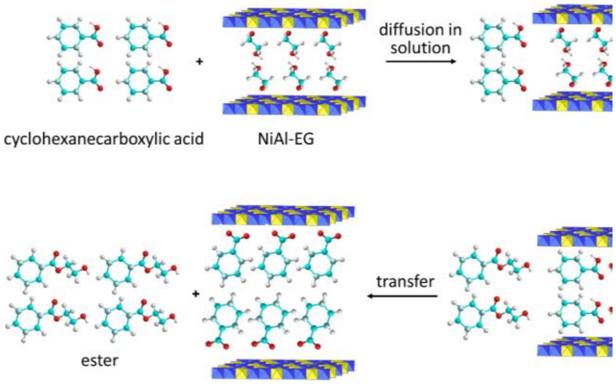
[13] S.C. Guo, D.Q. Li, W.F. Zhang, M. Pu, D.G. Evans, X. Duan, Preparation of an anionicazo pigment-pillared layered double hydroxide and the thermo- and photostability of the resulting intercalated material, J. Solid State Chem. 177 (2004) 4597-4604.

[14] E. Narita, P. Kaviratna, T.J. Pinnavaia, Synthesis of heteropolyoxometalate pillared layered double hydroxides via calcined zinc-aluminium oxide precursors, Chem. Lett. 20 (1991) 805-808.

[15] X. Lei, F. Zhang, L. Yang, X. Guo, Y. Tian, S. Fu, F. Li, D.G. Evans, X. Duan, Highly crystalline activated layered double hydroxides as solid acid-base catalysts, Aiche J. 53 (2007) 932-940.

[16] Q.S. Luo, L. Li, Z.X. Wang, X. Duan, Theoretical study of the layer-anion interactions in magnesium aluminum layered double hydroxides, Chin. J. Inorg. Chem 17 (2001) 835-842.

[17] Q. Chen, S. Shi, X. Liu, L. Jin, M. Wei, Studies on the oxidation reaction of L-cysteine in a confined matrix of layered double hydroxides, Chem. Eng. J. 153 (2009) 175-182.



Graphical abstract

An intracrystalline catalytic esterification between EG anions pre-immobilized in layered double hydroxide and cyclohexanecarboxylic acid was constructed. Apparently higher deacidification ratio than that of the bulk catalytic reaction was obtained.

Highlights:

- Ethylene glycol (EG) intercalated LDH was synthesized.
- Intracrystalline esterification occurs between EG in LDH and cyclohexanecarboxylic acid.
- LDH sheets act as esterification catalyst.
- This reaction shows much higher deacidification efficiency than bulk reaction.