Electronic Supplementary Material

Study on the cataluminescence of propylene oxide on FeNi layered double hydroxides/graphene oxide

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Preparation of catalysts

Synthesis of Graphene Oxide. Graphene oxide was prepared according to Hummers' method with a few modifications. 70 mL strong sulfuric acid was added into 3.0 g natural graphite, and then 1.5 g sodium nitrate was added. The mixture was set in the ice bath and kept stirring. Under vigorous agitation, 9.0 g potassium permanganate was added slowly into the solution to keep the temperature under 10℃ and stirred for 90 min. Then the system was transferred to water bath at 35℃-40℃ and stirred for another 90 min. After that, 500 mL deionizedwater was added into the solution and then stirred for 30 min at 95℃. After that, 20 mL H_2O_2 (30%) was added into the solution. The composite was filtered and washed with HCl aqueous solution(1:10) to remove the impurities followed by washing with deionizedwater until the pH of solution is neutral. To exfoliate the oxidized graphite,the product was treated with the ultrasonic bath for 2 h and then was freeze dried to obtain graphene oxide.

Synthesis of FeNi LDH. A series of LDH with different molarratio of Fe and Ni (1:3, 1:4, 1:6, 1:8, 1:10) were prepared, take LDH (Fe/Ni = 1:6) for example. 0.426 mL 1 mol/L $Fe(NO_3)_3$ $9H_2O$ and 2.56 mL 1 mol/L $Ni(NO_3)_2$ $6H_2O$ were mixed in 60 mL deionizedwater in a beaker. Then 5 mL 0.5 mol/L urea aqueous solution and 2 mL 0.01 mol/L trisodium citrate solution were successively added into the mixture with magnetic stirring for 30 min. And then the solution was transferred into a 100 mL Teflon lined stainless steel autoclave. After reacting at 150℃ for 48 h, the FeNi LDH was centrifuged and washed with deionizedwater for several times and dried in the oven for 12 h.

Synthesis of FeNi LDH/GO. The synthesis of FeNi LDH/GO was similar with FeNi LDH, except for the addition of different amount of GO (1.5×10^{-2}, 2.5×10^{-2}, 5×10^{-2},

10×10^{-2}, 15×10^{-2}g) into the precursor solution before transferring to the autoclave.
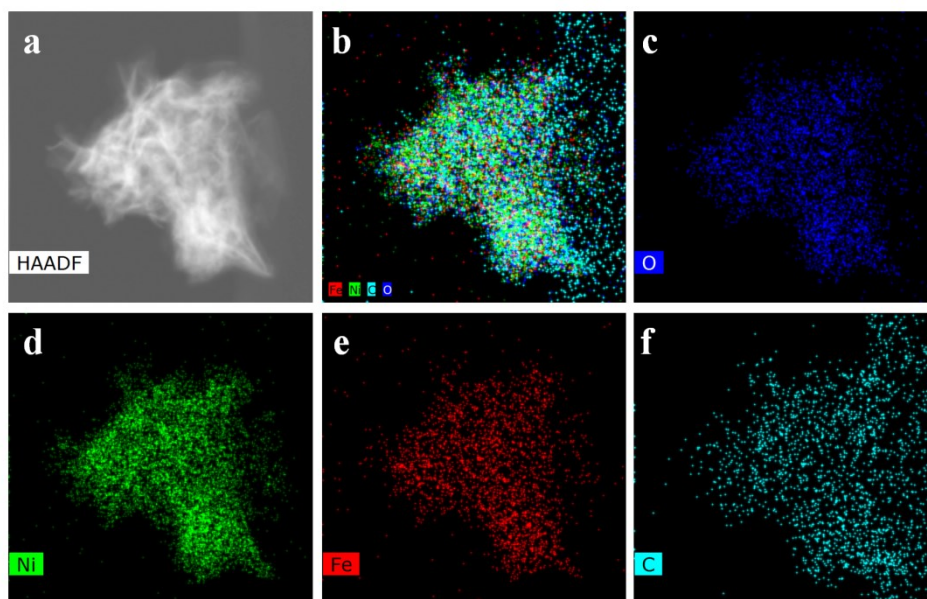

Fig. S1 Energy dispersive X-ray spectroscopy (EDS) of FeNi LDH/GO. (a) the high-angle annular dark field figure of FeNi LDH/GO; (b) the overlapping of Fe, Ni, C and O element; (c-f) the distribution of O, Ni, Fe and C element, respectively.

GO shows a characteristics peak at 9.8°, corresponding to (002) diffraction peak. The peaks at $2\theta = 11.4°$, 23.9° and 34.5° correspond to the (003), (006) and (009) diffraction peaks respectively, which is consistent with that reported about LDH. For LDH/GO composite, (002) diffraction peaks of GO were invisible, which might due to the small content or the broken stacking structure of GO (**Fig. S2a**). The FTIR spectra of GO, FeNi LDH and FeNi LDH/GO composites were displayed in **Fig. S2b**. As for GO, typical bands of oxygen containing functional groups at 3427 cm^{-1}, 1626 cm^{-1}, 1224 cm^{-1}, 1056 cm^{-1} can be observed. In LDH, the wide absorption band at around 3500 cm^{-1} was attributed to the O-Hstretching vibration of the water inserted between the layers, and the O-H bending vibration is at 1632 cm^{-1}. The absorption band at 1351 cm^{-1} should be assigned to CO_3^{2-} between the layers. (**Fig.**

S2c) The degradation of LDH/GO composites before 120 ℃ should be attributed to desorption of physical absorbed water on the surface of the material. At the range of 120℃ to 220℃, the thermogravimetric curve was relatively smooth and no obvious degradation was observed compared to LDH's; at around 230℃ there was a sharp mass loss, which belonged to the dehydroxylation of chemisorbed water embedded between the layers. The result indicates that the structure of FeNi LDH/GO could maintain stable under 210℃ in the air.
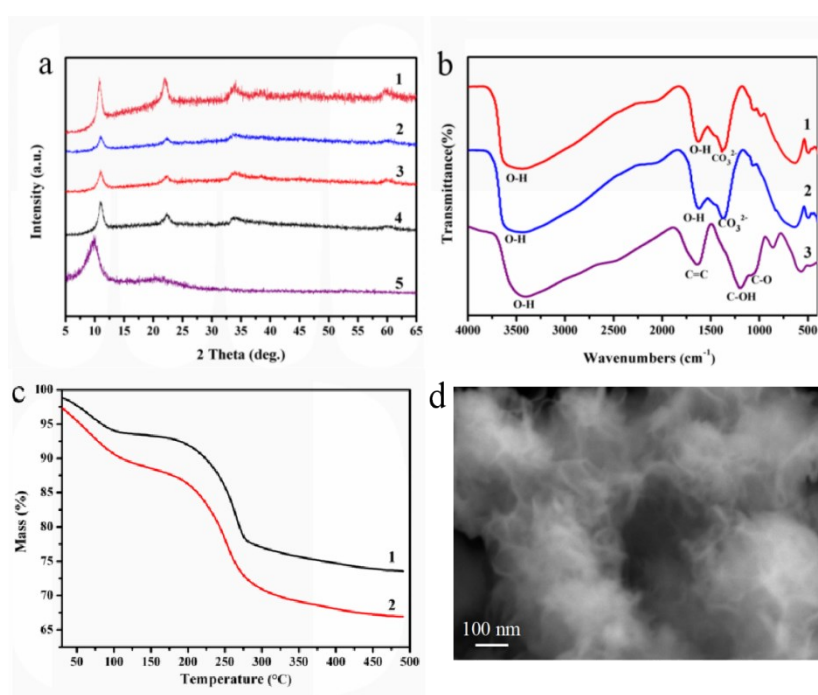

Fig. S2 (a) XRD of (1) FeNi LDH/GO, (2) FeNi LDH(Fe:Ni = 1:10), (3) FeNi LDH(Fe:Ni = 1:8), (4) FeNi LDH(Fe:Ni = 1:6), (5) pure GO; (b) FTIR spectra of (1) FeNi LDH, (2) FeNi LDH/GO and (3) GO; (c) Thermogravimetry curve (detected in the air atmosphere) of (1) FeNi LDH/GOand (2) FeNi LDH; (d) SEM image of FeNi LDH/GO after CTL reaction.
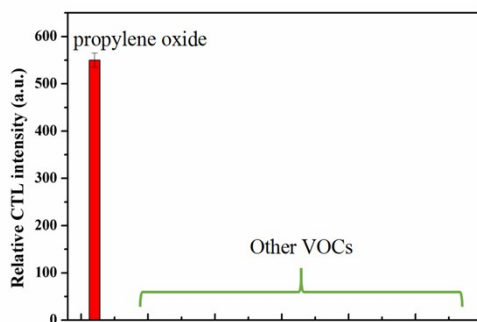
Fig. S3 CTL response of 31 VOCs on the surface of FeNi LDH/GO (the detecting VOCs including propylene oxide, acetone, ethanol, methanol, n-butanol, isobutanol, n-hexanol, benzene, toluene, n-hexane, formaldehyde, acetaldehyde, acetic acid, anisole, methyl benzoate, ethyl benzoate, phenethyl acetate, ethyl acetate, ethyl propionate, butyl acetate, methyl acrylate, propylene glycol methyl ether, ethylene glycol ether, ethylene glycol propyl ether, methyl sulfide, dichloromethane, propylene glycol, isooctane, n-octane, n-butyl ether, cyclohexane with the concentration of 300 mg/L).
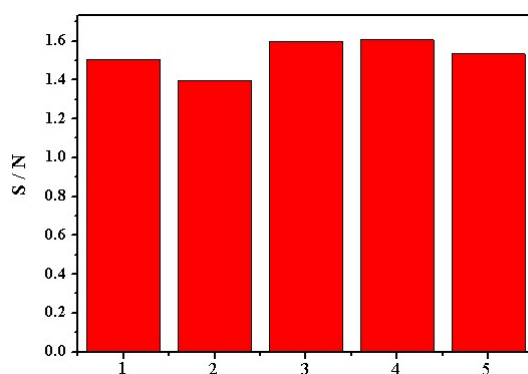

Fig. S4 CTL response of propylene oxide on the surface of graphene oxide (propylene oxide concentration: 300 mg/L; wavelength: 535 nm;working temperature: 210℃; flow rate of carrier gas: 0.3 L/min)

The retention time of the intermediate products

[1] Carbon dioxide (1.411 min), [2] aldehyde(1.479 min), [3] ethyl alcohol (1.604 min), [4] propylene oxide (1.705 min), [5] acetic acid (1.836 min), [6] allyl alcohol (1.955 min), [7] 2-methyl-1,3-pentanediol (2.027 min), [8] butenal (2.096 min), [9] 2,3-butanedione (2.269 min), [10] propylene formate (2.423 min), [11] trichloromethane (2.629 min), [12] 4-methyl-1,3-Dioxolane (3.166 min), [13] 2-methyl-1,3-Dioxane (3.694 min), [14] 2-methyl-1,3-Dioxane (3.956 min), [15] propylene acetate (4.074 min), [16] propyl acetate (4.501 min), [17] 2,2,4-trimethyl-1,3-Dioxolane (4.761 min), [18] 2-ethyl-4-methyl-1,3-Dioxolane (7.584 min), [19] 2-ethyl-4-methyl-1,3-Dioxolane (8.169 min), [20] allyl propionate (8.511 min), [21] 2,5-dimethyl-1,4-Dioxane (8.692 min), [22] 2,5-dimethyl-1,4-Dioxane (8.954 min).

Table S1. A summary on recently reported-methods for the determination of propylene oxide

Method	Sensing material	LOD (mg/L)	Linear range (mg/L)	Response time (s)	Interference elimination (spices of VOCs)	Ref.
GC	-	60 ng/m^3	-	-	-	[31]
CTL	CeO$_2$	0.9 mg/L	10 - 150	2	10	[32]
CTL	TiO$_2$ - Y$_2$O$_3$	1.25 mg/L	4.5 - 1375	-	18	[33]
CTL	FeNi LDH/GO	4.15 mg/L	8.3 - 415	1	30	this work

Table S2. Determination of propylene oxide in spiking samples with both CTL and GC

	methods (n=3)		
Sample	CTL method (mg/L)	GC method (mg/L)	Relative Error (%)
Sample 1	26.5 ± 0.1	25.8 ± 0.1	2.7
Sample 2	24.9 ± 0.3	23.3 ± 0.1	6.8

Computational details

Our computations are based on the first-principles density functional theory (DFT) approach within the generalized gradient approximation (GGA) method.[1] Vienna ab initio Simulation Package[2] has been employed throughout the study. Here, the valence electronic states are expanded in a set of periodic plane waves, and the interaction amid core electrons and valence electrons is implemented through the projector augmented wave method.[3] Perdew-Burke-Ernzerhof[4] parametrized GGA functionals are utilized to describe theexchange-correlation interactions. The wave functions were expanded into a basis set of plane waves with a kinetic energy cutoff of 400 eV. Ionic relaxations were carried out until the atomic forces were converged to 0.05 eV/Åby theBFGS optimization algorithm implemented in Atomic Simulation Environment, and the convergence threshold for self-consistence-field iteration was set at 10^{-4} eV. For geometry and cell optimizations of LDH, a $12 \times 12 \times 1$ k-point mesh for the primitive LDH unit cell was used.

Standard DFT has some problems to describe appropriately the strong correlation between d electrons. To address these issues, intra-site Coulomb repulsion U-term was incorporated, resulting into the so-called DFT+U method[5]. Specifically, the rotationally

invariant approach to the GGA+U was employed[6].The following values of the U parameter: U = 3.0 eV for the Fe and Ni 3d electrons[7] were applied.

A relative large supercell of LDH surface was utilized to accommodate the adsorbate, which was modelled as a single-layer $p(4 \times 4)$ periodic slab consisting of 80 atoms with a 30 Å vacuum between slabs. During geometry optimization, all of atoms were allowed to relax. The Brillouin zone was sampled at the Gamma point.The transition states were calculated using the double-ended surface walking method withLasp software[8].

The structure of adsorbates and the adsorption site with the catalyst was optimized and presented as followed, in which the bond length and the adsorption atom (with "*") of the molecular were shown.
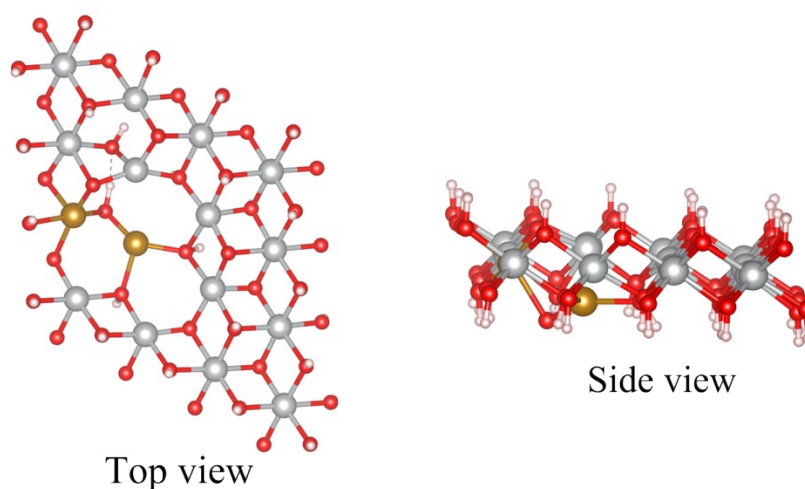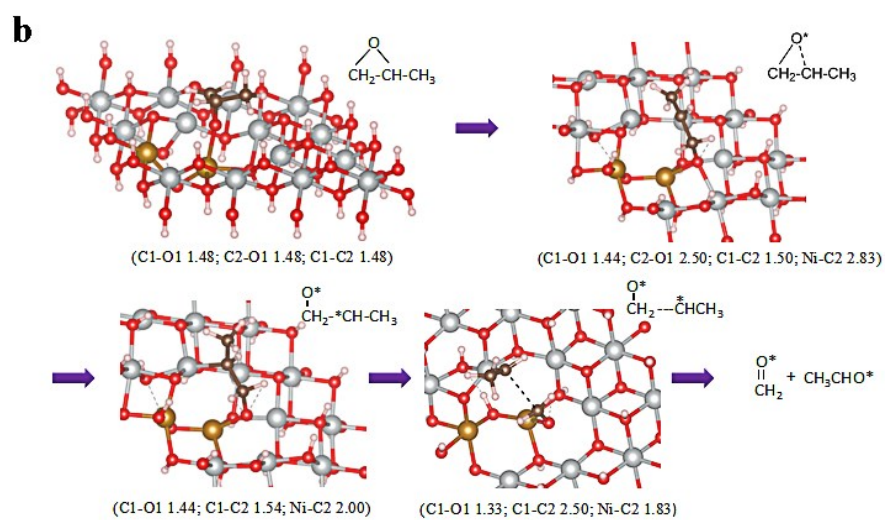

Top view

Side view

Fig.S5 Top view (left) and side view (right) of the modelled single-layer of LDH (4 × 4), including Fe atom(golden), Ni atom (silver), O atom (red), and H atom (pink).

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a

(C1-O1 1.99; C2-O1 1.45; C1-C2 1.47; Ni-C1 2.90)

(C2-O1 1.43; C1-C2 1.52; Ni-C1 1.92)

(C1-C2 2.63 ; C2-O1 1.28; Ni-C1 1.79)

(C1-C2 3.39 ; C2-O1 1.28; Ni-C1 1.82)

b

(C1-O1 1.48; C2-O1 1.48; C1-C2 1.48)

(C1-O1 1.44; C2-O1 2.50; C1-C2 1.50; Ni-C2 2.83)

(C1-O1 1.44; C1-C2 1.54; Ni-C2 2.00)

(C1-O1 1.33; C1-C2 2.50; Ni-C2 1.83)

c

(C1-O1 1.48; C2-O1 1.48; C1-C2 1.48)

(C1-O1 1.44; C2-O1 2.50; C1-C2 1.50; Ni-C2 2.83)

(C1-O1 1.44; C1-C2 1.54; Ni-C2 2.00)

(C1-O1 1.35; C1-C2 1.42; Ni-C2 3.22 C1-H 1.31; C2-H 1.56)

d

C1-O1 1.48; C2-O1 1.48; C1-C2 1.48

C1-O1 1.44; C2-O1 1.98; C1-C2 1.46

C1-O1 1.45; C1-C2 1.48

C1-O1 1.34; C1-C2 1.44; C1-H 1.24; C2-H 1.53

e

C1-O1 1.48; C2-O1 1.48; C1-C2 1.48

C1-O1 1.45; C1-C2 1.48

C1-O1 1.45; C1-C2 1.48

C3-H 1.36; O-H 1.37; C3-C2 1.41

C3-H 2.94; O-H 0.98; C3-C2 1.34

C3-H 1.19; O-H 1.60; C3-C2 1.44

C3-H 2.94; O-H 0.98; C3-C2 1.34

O-H 1.52; Olat-H 1.05; C1-O 1.43; Fe-O 2.11

Fig. S6 Optimized structure of adsorbates and the adsorption site with the catalyst, in which the bond length and the adsorption atom (with "*") of the molecular were shown. The optimized reaction processes were presented as followed: (a) R_4; (b) R_8; (c) R_7, (d) R_{10}; (e) R_{11} and R_{12}.
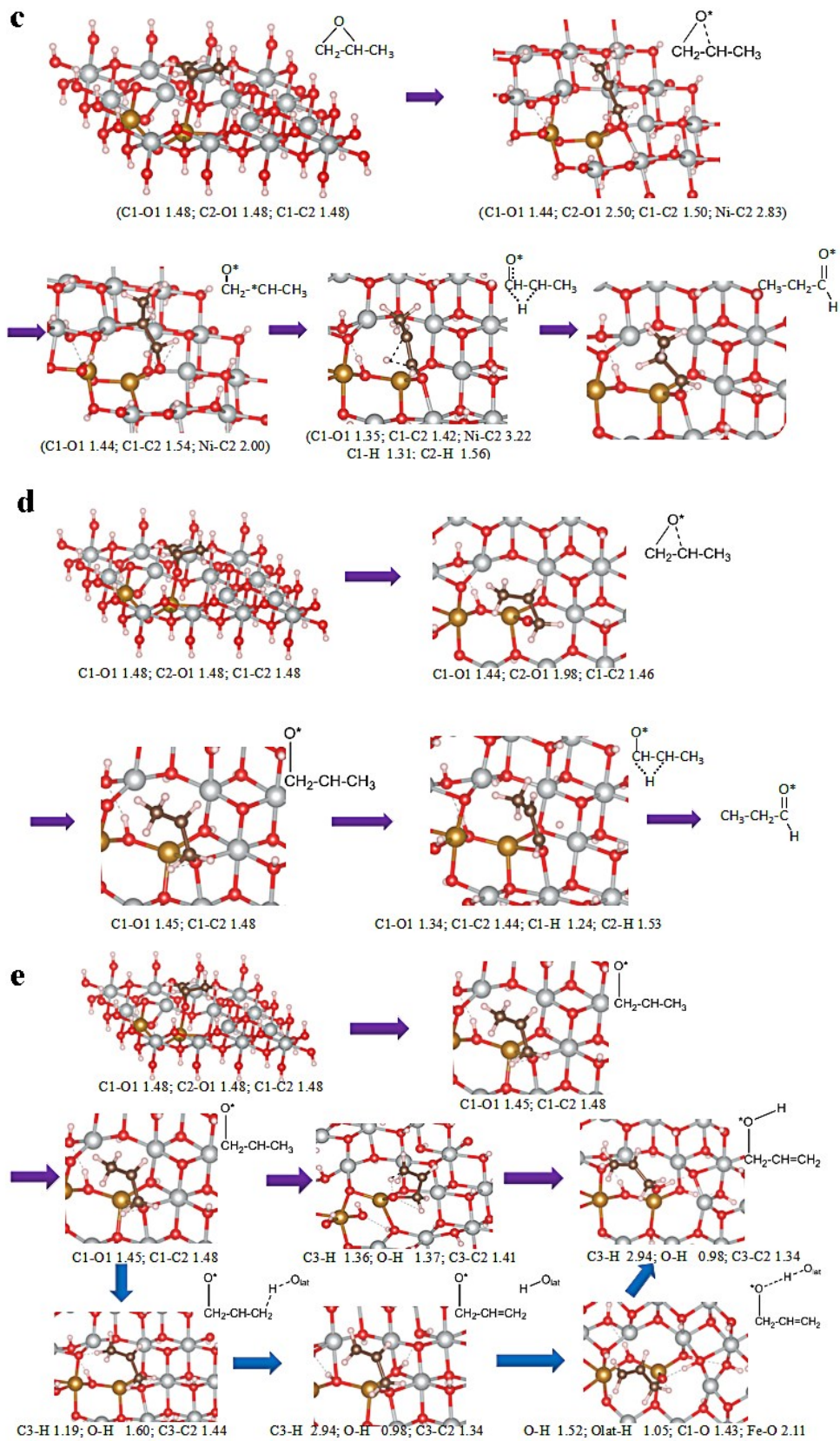
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