



Accepted Manuscript

View Article Online View Journal

This article can be cited before page numbers have been issued, to do this please use: S. Wang, S. Yin, G. Chen, L. Li and H. Zhang, *Catal. Sci. Technol.*, 2016, DOI: 10.1039/C6CY00186F.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/catalysis

Cite this: DOI: 10.1039/c0xx00000x

Nearly atomic precise gold nanoclusters on nickel-based layered double hydroxides for extraordinarily efficient aerobic oxidation of alcohols

Shuai Wang, Shuangtao Yin, Gaowen Chen, Lun Li and Hui Zhang*

s Received (in XXX, XXX) Xth XXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX DOI: 10.1039/b000000x

A series of nickel-based layered double hydroxides supported nearly atomic precise Au₂₅ nanoclusters catalysts especially Au₂₅/Ni_xAl-LDH systems (x=Ni/Al, 2, 3, 4) were fabricated via modified electrostatic adsorption of captopril-capped clusters Au₂₅Capt₁₈ onto the predispersed positively-charged Ni_xAl-LDH 10 supports followed proper calcination. Detailed characterizations show that the ultrafine gold clusters of ~0.9 nm were well-dispersed on the edge sites of hexagonal plate-like particles of Ni_x Al-LDH (x=2, 3) originated from their ordered LDH layers with more Ni-OH sites and strong Au-LDH synergy, while slightly aggregated to ~1.1 nm on the irregular Ni₄Al-LDH due to its poor layer structure along with doped nickel oxide. The catalysts exhibit excellent activity for selective oxidation of 1-phenylethanol to 15 acetophenone with molecular oxygen under base-free, and the activity follows an increased order of $Au_{25}/Ni_4Al-LDH < Au_{25}/Ni_2Al-LDH < Au_{25}/Ni_3Al-LDH$. The $Au_{25}/Ni_3Al-LDH$ shows the highest activity with TOF of 6780 h^{-1} in toluene and 118500 h^{-1} in solvent-free and can be applied for a wide range of alcohols, mainly ascribed to the ultrafine gold clusters and the strongest gold-LDH interaction associated with the highly ordered Ni₃Al-LDH layers. Similar regularity is found in the Au₂₅/Ni_xMn-LDH ²⁰ and Au₂₅/Ni_{3-x}Mn_xFe-LDH systems. The Au₂₅/Ni₃Al-LDH can be reused five times without loss of activity. The least-square fit analysis yields the rate constant (k) and apparent activation energy (E_a) of Au₂₅/Ni_xAl-LDH catalysts for 1-phenylethanol oxidation, and the order of k and E_a values act in accordance with their reactivities.

Introduction

- 25 Since Haruta et al.¹ reported gold nanoparticles (3.6-8 nm) dispersed on transition metal oxides exhibited high activity in the low-temperature oxidation of CO by molecular oxygen in 1989, supported gold catalysts have been widely explored for a variety of organic reactions including selective hydrogenation of nitro ³⁰ compounds² and α , β -unsaturated carbonyl compounds,³ C-C coupling,⁴ hydrochlorination of acetylene,⁵ and oxidation of alcohols.⁶ Therein, alcohols oxidized to carbonyl compounds is one of the most essential reaction in organic synthesis. The
- traditional alcohol oxidation technology involves stoichiometric 35 quantities of inorganic oxidants, such as permanganate and dichromate, which produces a large amount of wastes containing toxic heavy metals and causes serious environmental problem. Moreover, the additional base (e.g., NaOH, K₂CO₃) is needed while using Au nanoparticles (NPs) catalysts whether colloidal
- 40 polymer-protected Au NPs^{7,8} or supported Au NPs^{6,9} in liquidphase aerobic alcohol oxidation, which unavoidably leads to reactor corrosion and environmental pollutions. From the view of green chemistry, it has great theoretical and practical significance to develop a route for the oxidation of alcohols with molecular
- 45 oxygen upon a heterogeneous bifunctional catalyst combining Au nanoparticles with a solid base.

Catalysis Science & Technology Accepted Manuscript Another important aspect is that the reactivity for alcohol oxidation catalyzed by Au catalysts is generally increased with reduced sizes of Au NPs.^{7,10} Tsukuda et al.¹⁰ reported a set of 50 poly-(N-vinyl-2-pyrrolidone)-stabilised Au clusters with sizes in 1.3-9.5 nm for oxidative dehydrogenation of *p*-hydroxybenzyl alcohol in H₂O with K₂CO₃ and found that the activity increased slowly with Au clusters' sizes reducing from 9.5 to ~4 nm and then increased rapidly with further reduced size of Au clusters. 55 Corma et al.¹¹ and Prati et al.¹² prepared Au/CeO₂ and Au/NiO, respectively, by exploring the combinations of small-size Au (<5 nm) and nanocrystalline metal oxides (5 nm), which turned out to obtain highly active and selective catalysts for the oxidation of alcohols under base-free condition ascribing to the synergy 60 between Au and nanoscaled supports CeO₂ or NiO. However, the required procedures for preparing fine nanoscaled support (for Au/CeO₂) and the requirement of higher O₂ pressure (for Au/NiO) Layered double hydroxides (LDH), a layered anionic clay

would limit their wide application.

65 consisting of a positively charged two-dimensional brucite layer

with interlayer anions such as carbonate, hydroxide, and/or other desired anions,^{13,14} has progressively received attention as

catalysts or supports due to its unique surface acid-basic property

and potential redox nature.^{15,16} Kaneda et al.¹⁷ firstly reported

upon varied reductant (KBH4, H2, hydrazine) and found that their

70 Au/MgAl-LDH catalysts with Au NPs' sizes within 2.7-4.6 nm

Published on 31 March 2016. Downloaded by George Washington University on 05/04/2016 19:18:07

activities for 1-phenylethanol oxidation is increased with reduced Au NPs. Wang *et al.*¹⁸ prepared Au/MgAl-LDH catalysts with mean Au NPs' sizes in 2.1-21 nm by deposition-precipitation method and studied their oxidant-free dehydrogenation properties ⁵ of benzyl alcohol, showing that the activity is increased slightly

- with Au particle reduced from 12 to ~4 nm while increased steeply with the mean Au size further reduced to 2.1 nm. Li *et al.*¹⁹ reported transition metals modified MgAl-LDH (M-HT, M= Cr^{3+} , Co^{2+} , Ni^{2+}) by calcination-reconstruction steps for Au-
- ¹⁰ loaded catalysts (2.7-3.9 nm) and found Au/Cr-HT bearing the highest activity (TOF=930 h⁻¹) for benzyl alcohol oxidation. Zhao et al.²⁰ reported the Au/yNiAl-LDHs catalysts with Au NPs of ~5 nm by a modified in situ reduction-deposition step, in which AuNPs uniformly distributed on Ni–Al LDHs were shown to be ¹⁵ efficient catalysts for the selective oxidation of alcohols to the corresponding aldehydes or ketones under base-free conditions with O₂. Clearly, further reduced size of Au active phase upon modified method for greatly improved alcohol oxidation activity is highly desired.
- 20 Gold clusters composed of less than 100 atoms with the size <2 nm quite different from Au nanocrystals (>2 nm) due to the distinct quantum-size effect,²¹ make this type of nanomaterial very promising in developing new generation of catalysts.²² Gold clusters-supported catalysts were successful in catalyzing varied 25 type of oxidation reactions, such as oxidation of primary and secondary alcohols,^{23,24} alkenes (C=C bonds),²⁵ and alkanes (C-H bonds).²⁶ Among the well-defined Au clusters, thiolate-capped Au₂₅(SR)₁₈ clusters, composed of an icosahedral Au₁₃ core and a shell of twelve Au atoms that are face-capped on the Au₁₃ core, ³⁰ have been extensively studied.^{21,27} Tsukuda et al.²⁶ reported Au_n clusters (n=10, 18, 25, 39) loaded on hydroxyapatite with average Au_n diameters of 1.0 ± 0.4 - 1.1 ± 0.5 nm exhibiting the excellent activity for cyclohexane oxidation by O2 and TBHP. The Au₂₅(SR)₁₈ clusters can also be loaded on other metal oxides, ³⁵ such as TiO₂²⁸, CeO₂²⁹, and MgO³⁰, showing variously enhanced activity for varied catalytic processes. In our previous work, we first reported the LDH-loaded Au nanoclusters (NCs) catalysts with glutathione-capped AuNCs for alcohols oxidation and found AuNCs/Ni₃Al-LDH giving the highest 1-phenylethanol oxidation 40 activity.31 However, the pristine AuNCs and those in the AuNCs/LDH catalysts show the average sizes of $1.5 \pm 0.5 - 2.0 \pm$ 0.7 nm, obviously larger than the critical size of Au_{25} clusters
- 0.7 nm, obviously larger than the critical size of Au₂₅ clusters (~0.9 nm), and the unique roles of the transition-metal-based LDH supports are still controversial, and the nature of Au-45 clusters-LDH synergy are not clear.

In the present work, we successfully synthesize a series of nearly atomic precise Ni-based LDH supported gold clusters catalysts (~0.9 nm) by a modified electrostatic adsorption strategy from a atomically precise captopril-capped clusters Au₂₅Capt₁₈ in 50 order to deeply study the natural effect of the LDH supports on

alcohol oxidation and shed new light on the synergy between Au_{25} clusters and the supports. The reaction rate constant (*k*) and apparent activation energy (E_a) of 1-phenylethanol oxidation over the Au_{25}/Ni_xAl -LDH catalysts were determined and discussed.

55 Experimental section

Chemicals

Chloroauric acid tetrahydrate (HAuCl₄'4H₂O, > 99.9%, AR) and sodium borohydride (NaBH₄, 99.5%, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd., tetraoctylammonium ⁶⁰ bromide (TOABr, 98%, AR) from J&K, captopril (C₉H₁₅NO₃S, 99%, AR) from Changzhou Pharmaceutical Factory, and methanol (CH₃OH, \geq 99.9%, HPLC) from Tianjin Shield Specialty Chemical Ltd. Co. All of the substrate alcohols (AR) were purchased from Aladdin. The deionized water with the ⁶⁵ resistivity of > 18.25 MΩ was used throughout the experiments.

Preparation of Au₂₅Capt₁₈

Water-soluble captopril-capped Au25 nanoclusters were prepared using a size-focusing synthetic methodology according to the previous report by Jin et al.³² Typically, 8.23 mL HAuCl₄·4H₂O 70 (10 mg/mL in methanol) was added to 1.77 mL methanol in a 25 mL single-necked flask while vigorously stirring at 25°C. Then, TOABr (0.23 mmol) was added to the flask and the solution color changes from yellow to deep red. After 20 min, captopril (1 mmol dissolved in 5 mL methanol) was rapidly injected into the 75 reaction mixture under vigorously stirring. The solution quickly becomes white. After 30 min, an aq. solution of 5 mL of NaBH₄ (2 mmol dissolved in 5 mL of ice cold water) was added rapidly to the reaction mixture under vigorous stirring and the solution immediately turned to brown-blackish (see photos in Fig. S1). 80 The reaction was allowed to proceed for 8 h and the reaction mixture was centrifuged (5000 r/min, 20 min) to remove unreacted, insoluble Au(I):SR intermediate complexs. The supernatant was collected and the solvent was removed by rotary evaporation (30 °C, 20 min) followed by adding ethanol (20 mL) 85 and standing overnight to obtain the brown-black precipitate. The precipitate was dried in vacuum at 30 °C giving raw product. Then, the raw product was extracted with minimum amounts of methanol several times followed by adding ethanol (30 mL) and centrifuging (3000 r/min, 10 min) to obtain brown-blackish ⁹⁰ precipitate, which was dried at 30 °C in vacuum overnight giving brown-blackish product Au₂₅Capt₁₈.

Preparation of layered double hydroxides (LDH) supports

Carbonate-containing Ni_xAl-LDH supports were prepared by a single-drop coprecipitation step. In detail, a 50 mL aq. solution ⁹⁵ containing Ni(NO₃)₂'6H₂O and varied amounts of Al(NO₃)₃'9H₂O upon designed Ni/Al molar ratio x (= 2, 3, or 4) with a total cationic concentration of 1.0 M was added dropwise into a 250 mL round-bottle flask containing 50 mL mixed alkaline solution of NaOH and Na₂CO₃ ([CO₃²⁻]/[Al³⁺] = 2, [OH⁻]/[Al³⁺ + Ni²⁺] = ¹⁰⁰ 1.6) under vigorous stirring. The resultant was aged at 120 °C for 6 h, then centrifuged and washed by deionized water until pH ~7 and dried at 60 °C overnight giving the Ni_xAl-LDH supports. Ni(OH)₂ was also prepared by the similar step without Al(NO₃)₃'9H₂O employed for comparison.

Ni_xMn-LDH supports were obtained by a double-drop coprecipitation step. A 100 mL aq. solution with Mn(CH₃COO)₂'4H₂O (0.006 mol) and varied amounts of Ni(NO₃)₂'6H₂O upon Ni/Mn ratio (x = 2, 3) and a 100 mL alkaline solution of NaOH and Na₂CO₃ ([CO₃²⁻]/[Mn²⁺] = 2, 110 [OH⁻]/[Mn²⁺+Ni²⁺]=1.6) was simultaneously added dropwise into a 500 mL round-bottle flask with 100 mL deionized water under vigorous stirring keeping the reaction pH of 10.

Catalysis Science & Technology Accepted Manuscrip

The resultant was aged at 25 °C for 24 h, then centrifuged and washed by deionized water until pH ~7 and dried at 60 °C for 8 h giving the Ni_xMn-LDH supports. Ni_{3-x}Mn_xFe-LDH (x = 0.5, 0.8, 1) supports were also prepared by the ⁵ double-drop coprecipitation step. A 100 mL aq. solution with 0.006 mol Mn(CH₃COO)₂'4H₂O and varied amounts of Ni(NO₃)₂'6H₂O and Fe(NO₃)₃'9H₂O and a 100 mL alkaline solution (NaOH and Na₂CO₃, $[CO_3^{2^-}]/[Fe^{3+}] = 2$, $[OH^-]/[Mn^{2+} + Ni^{2+} + Fe^{3+}] = 1.6$) was simultaneously added ¹⁰ dropwise into a 500 mL flask containing 100 mL deionized water under vigorous stirring keeping the reaction pH of 10. The resultant was aged at 65 °C for 24 h, then centrifuged and washed by deionized water until the pH ~7 and dried at 60 °C for 24 h giving the Ni_{3-x}Mn_xFe-LDH supports.

15 Preparation of LDH supported Au₂₅ clusters catalysts

The LDH loaded Au₂₅ clusters catalysts were prepared by a modified electrostatic adsorption strategy. Firstly, 1.25 g Ni_xAl-LDH support was ultrasonically dispersed into 50 mL deionized water for 10 min to obtain a buffer suspension (pH ~7.98, 7.7, ²⁰ 7.4). Then, 10 mL of Au₂₅Capt₁₈ solution (3.5 mg dispersed in 10 mL deionized water, pH ~6.67) was added into the above suspension under vigorous stirring for 10 min at room temperature. The mixture was collected by centrifugation (4000 rpm, 3 min) and then dried at 60 °C overnight giving the catalyst ²⁵ precursors Au₂₅Capt₁₈/Ni_xAl-LDH. Secondly, the precursors were calcined at 300 °C for 2 h in air giving the Au₂₅/Ni_xAl-LDH catalysts. Scheme 1 depicts the design schematic of Au₂₅/Ni_xAl-LDH and Au₂₅/Ni_{3-x}Mn_xFe-LDH and reference catalyst Au₂₅/Ni(OH)₂ were ³⁰ prepared in the same way.



Scheme 1 Design schematic of the Au₂₅/LDH catalysts using Ni_xAl-LDH system as example.

Characterization

- ³⁵ The UV-vis spectra were obtained on a Shimadzu UV-2501PC spectrophotometer. The thermogravimetric analysis (TG) was performed on a Mettler-Toledo TGA/DSC 1/1100 ST thermal analyzer. Electrospray ionization mass spectra (ESI-MS) were recorded using a Waters Xevo G2S quadrupole time-of-flight (Q-40 TOF) mass spectrometer. The sample was dispersed in methanol and infused at a flow rate of 5 µL/min. The capillary voltage was set as 2.50 kV. The source temperature and desolvation temperature were 120 °C and 500 °C, respectively. The desolvation gas flow was 800 L/h. The determination of isoelectronic point (pI) of the samples was obtained from the Zeta potential analysis on a Malvern Zetasizer Nano ZS instrument
- equipped with a multipurpose autotitrator (MPT-2). Powder Xray diffraction (XRD) patterns were taken on a Shimadzu XRD-6000 diffractometer using Cu K α radiation (1.5418 Å, 40 kV, 30
- ⁵⁰ mA). The samples, as unoriented powders, were step-scanned in steps of $0.02^{\circ} (2\theta)$ in the range of $3-70^{\circ}$ using a count time of 4 s per step. Elemental analysis for metal ions was done on a Shimadzu ICPS-7500 inductively coupled plasma atomic emission spectroscopy (ICP-AES) after dissolving sample in
- ⁵⁵ chloroazotic acid (1 mL) followed diluted to 10 mL using deionized water. Scanning electron microscopy (SEM) along with elements mapping were recorded on a Hitachi S-3500N apparatus at 20 kV. High resolution TEM was recorded on a JEM 2010 transmission electron microscope at 200 kV. The high-angle
 ⁶⁰ annular dark-field scanning transmission electron microscopy
- (HAADF-STEM) along with energy dispersive X-ray spectra (EDX) were recorded on a JEOL JEM-2100F transmission electron microscope equipped with a digitally processed STEM

- imaging system operating at 200 kV. The samples were ⁶⁵ ultrasonically dispersed into ethanol-water solution (v/v = 1/1) for 2 min and put two drops on a holey carbon film supported by a copper grid. The electron probe size was approximately 0.5 nm. The HAADF-STEM image was recorded for 8.2 s with a digital resolution of 512 × 512 pixels.
- Fourier transform infrared spectra were obtained on a Bruker Vector-22 FT-IR spectrophotometer using KBr pellet technique (sample/KBr = 1/100). The UV-Vis diffusion reflection spectra (DRS) were recorded on a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer. The spectra were collected at 220-800 nm 75 with BaSO₄ as a reference. Specific surface areas were obtained upon BET method from N₂ adsorption-desorption isotherms measured on a Quantachrome Autosorb-1C-VP system. The temperature-programmed surface reaction (TPSR) was carried out on a Thermo Fisher TPD/R/O 1110 instrument as follows. ⁸⁰ After the sample (55 mg) was activated at 200 °C for 2 h under helium stream (20 mL/min), it was cooled down to 40 °C and isopropanol vapor was introduced for adsorption at 40 °C for 60 min. After the sample was swept with helium stream for 60 min, the temperature was enhanced linearly with a rate of 10 °C/min in s the argon stream and the signals of H_2 (M/e = 2) were taken by an online mass spectrometry (Omnistar TM) simultaneously. The surface chemical compositions were studied on a VG ESCALAB-250 X-ray photoelectron spectrometer (XPS) at a base pressure in the analysis chamber of 2×10^{-9} Pa using a standard Al K α source 90 (1486.6 eV). The binding energy scale was referenced to the C 1s line of aliphatic carbon contamination (285.0 eV). The studies of CO molecules adsorbed on the catalyst were done combining with IR on a Nicolet 380 instrument containing a controlled

environment chamber equipped with CaF2 windows. The IR

spectra were recorded by using wafers in the form of selfsupporting pellet of sample mounted in a homemade ceramic cell. Prior to measurements, the samples were first heated to 100 $^{\circ}$ C at heating rate 5 $^{\circ}$ C/min in N₂ flow and kept for 1 h, then cooled to 5 50 $^{\circ}$ C. The sample was scanned to get a background, then

exposed to a CO flow for 1 h, followed the cell purging with N_2 for 30 min and the IR spectra were recorded in absorbance mode at 4 cm⁻¹ resolution upon averaging 64 scans.

Activity test

- ¹⁰ The liquid-phase aerobic oxidation of 1-phenylethanol was done using a 25 mL three-necked round-bottle flask with a reflux condenser under magnetic stirring. The substrate (5 mmol), solvent (toluene, 5 mL) and catalyst (Au: 0.01 mol%) were mixed in the flask and then heated to the reaction temperature (60, 70,
- ¹⁵ 80, 90 and 100 °C) with O₂ bubbling (20 mL/min) at atmospheric pressure. During the reaction, 0.2 mL aliquots were pipetted every 15 min, filtered (0.22 μ m) and analyzed by GC (Agilent 7890A) equipped with a flame ionisation detector and an Agilent J&W HP-5 (5% phenyl polysiloxane, 30 m × 0.25 mm × 0.25 μ m)
- ²⁰ capillary column. Biphenyl was used as an internal standard for quantitative analysis. The solvent-free oxidation of 1-phenylethanol was done as follow: 1-phenylethanol (100 mmol), catalyst (Au: 4.0×10^{-4} mol%), reaction temperature (120, 130, 140, 150 and 160 °C). After reaction, the sample was centrifuged ²⁵ and washed with toluene and dried at 60 °C overnight for next run.

Results and discussion

The successful synthesis of water-soluble Au₂₅Capt₁₈ clusters with high purity can be verified by FT-IR, UV-vis data and ESI-MS. The ligation of captopril in the form of the thiolate to the Au ³⁰ core was indicated by the absence of the IR band v(S-H) at 2567 cm⁻¹ in Au₂₅Capt₁₈ (Fig. S2A).¹⁴ The UV-vis spectrum of the original solution of Au₂₅Capt₁₈ (Fig. 1A(a)) shows an exponential-like decay from the UV region into the visible region while no surface plasmon resonance band at ~520 nm typical of ³⁵ Au NPs with diameters > 2 nm,²¹ implying the ultrafine clusters of the Au₂₅Capt₁₈ below 2.0 nm. Moreover, because of strong quantum size effects, the Au₂₅Capt₁₈ cluster shows multiple

- molecular-like transitions in the optical spectrum with at least three well-defined bands at 670, 450, and 400 nm (Fig. 1A). The 40 excited state at 670 nm corresponds to a LUMO \leftarrow HOMO transition, *i.e.*, essentially an intraband (sp \leftarrow sp) transition, which can be viewed as a transition entirely due to the electronic and geometric structure of the Au₁₃ core.²¹ The peak at 450 nm arises from mixed intraband (sp \leftarrow sp) and interband (sp \leftarrow d) transitions,
- ⁴⁵ and the peak at 400 nm principally from an interband transition (sp←d). Meanwhile, a broad shoulder at ~800 nm (spinforbidden) is observed and the 400 nm band is less pronounced, confirming that native Au₂₅Capt₁₈ clusters are indeed anionic.³³ The ESI-MS result further clearly suggest the obtained gold ⁵⁰ clusters to be Au₂₅Capt₁₈ (Fig. S2C).

The XRD pattern of $Au_{25}Capt_{18}$ (Fig. 1B) shows a relative strong peak at 37.5° (0.235 nm) and a very broad feature at 64.5°. Upon the peak width (full width at half maximum, FWHM in rad.) at 37.5°, the particle dimension can be tentatively estimated as 0.8

ss nm by the Debye-Scherrer formula, $D=0.9\lambda/(FWHM \cdot \cos\theta)$, where FWHM is 11° (0.19 rad.) and λ is 0.1542 nm. The HRTEM image of the sample with Au₂₅Capt₁₈ directly dispersed in water (Fig. 1E and F) shows that the Au cluster size is 1.5 ± 0.5 nm (on ~150 particles), slightly larger than the critical value of Au₂₅ ⁶⁰ cluster (~0.9 nm)²⁷, implying the assemblages of the ultrafine gold clusters formed by hydrogen bond between the protonated – CO₂H groups of the ligands.³⁴ To test this hypothesis and evaluate the core diameters of individual Au₂₅Capt₁₈ clusters, another sample with the Au₂₅Capt₁₈ initially dissolving in pH 7.9 ⁶⁵ buffer solution, in which most of the –CO₂H groups of the ligands are dissociated into –CO₂⁻ given the pK_a of 3.7 for –CO₂H in captopril.¹⁴ Then, the obtained HRTEM clearly reveals a dramatically reduced average Au core size of 0.9 ± 0.3 nm (on ~150 particles) (Fig. 1C and D), which is reasonably agreement 70 with the Scherrer dimension 0.8 nm and very close to ~0.9 nm of

Au₂₅ clusters in theory, indicating the significantly improved dispersibility and nearly atomically monodispersed Au₂₅Capt₁₈ clusters owing to the Coulomb repulsion,^{34,35} which is favorable for the synthesis of the LDH supported Au₂₅ clusters catalysts. ⁷⁵ The FFT images (insets in Fig. 1D and F) shows one-pair diffraction pot in a weak diffusive ring for the sample with Au₂₅Capt₁₈ dispersed in basic buffer instead of several bright diffraction spots for the sample with Au₂₅Capt₁₈ directly dispersed in water, also implying the ultrafine size of the ⁸⁰ Au₂₅Capt₁₈ in basic media.

Upon the Zeta potential analysis (Fig. S3), the isoelectric point (pI) of $Au_{25}Capt_{18}$ in the solution is *ca*. 5.66. When pH > pI, the proton of $-CO_2H$ group at the opposite side of the thiol group was dissociated to form $-CO_2^-$ with a negative electric potential ⁸⁵ formed on the surface of Au_{25} clusters. Such Au_{25} clusters can verify the high dispersion state without aggregation due to



Fig. 1 UV-vis (A) of original solution of $Au_{25}Capt_{18}$ (a) and supernatant after impregnation on LDH (b), XRD (B) of $Au_{25}Capt_{18}$, HRTEM of

4 | Journal Name, [year], [vol], 00-00

Au₂₅Capt₁₈ dispersed in basic buffer (C, D) and directly dispersed in water (E, F) (insets: the histogram of the size distribution and FFT).

electrostatic repulsion. When pH < pI, the Au₂₅ clusters surface turns to be electrostatically neutral to lose the driving force of ⁵ dispersion thus the hydrophobic interactions between Au₂₅ clusters predominate, considering the proton of the weak acid – CO₂H group of captopril cannot be ionized. While the pI of Ni_{*x*}Al-LDH supports with *x* = 2, 3, and 4 is determined as 9.3, 9.8 and 10.6, respectively, similar to previous report³¹. These results ¹⁰ imply that the negatively charged Au₂₅ clusters can be easily adsorbed on the positively charged LDH supports by electrostatic attraction at pH ~7-9 with high dispersibility. Meantime, the hydrogen bond between the -OH groups of LDHs and partial undissociated –CO₂H groups of the ligands may also contribute ¹⁵ to the monodispersion of Au₂₅ clusters on the LDH supports.

Then, during the synthesis process of the catalyst (Scheme 1), the LDH supports were carefully predispersed in water forming a basic buffer (pH~8.0), followed the desired amount of Au₂₅Capt₁₈ clusters were added. It was clearly seen that Au₂₅Capt₁₈ clusters ²⁰ were fast adsorbed on the surface of LDH (photos in Scheme 1), evidenced by the colourless supernatant, upon strong electrostatic attraction and hydrogen bonding between the negatively charged Au₂₅Capt₁₈ and the positively charged Ni_xAl-LDH nanoplates, forming the catalyst precursors Au₂₅Capt₁₈/Ni_xAl-LDH. As the ²⁵ TG plot of pure Au₂₅Capt₁₈ shows a constant weight loss of 43.6% at 300 °C (Fig. S2B), in good agreement with the theoretic content of ligands, the catalyst precursors were calcined at 300 °C to remove the ligands, giving the Au₂₅/Ni_xAl-LDH catalysts.

Fig. 2 presents the XRD patterns of the Au₂₅/Ni_xAl-LDH 30 catalysts compared with the precursors and the supports. Both the NixAl-LDH supports and the Au25Capt18/NixAl-LDH precursors show typical hexagonal crystal structure of LDH materials^{13,31} without other crystal phase. The characteristic reflections of the supports (Fig. 2(a₀,b₀,c₀)) and catalyst precursors (Fig. 2(a',b',c')) 35 show a series of (00*l*) peaks as sharp, symmetric, and strong lines at low 2θ angles, implying good crystallinity of the LDH moieties in Ni_xAl-LDH and Au₂₅Capt₁₈/Ni_xAl-LDH samples. The FWHM of (003) peak is increased with increasing Ni/Al ratio x, implying the reduced crystal size of LDH phase with increasing Ni content, 40 just reflected by the Scherrer dimensions (Table S1). The intensities of (110) and (113) peaks are enhanced with increasing Ni/Al ratios for the samples with x of 2 and 3, suggesting that the metal cations in the brucite-like layers become highly ordered with increasing Ni content, in accordance with their crystal sizes

- ⁴⁵ along (110) plane (Table S1). While those for the sample with Ni/Al ratio of 4 are inferior to those of x = 2 and 3, which is probably due to the formation of Ni(OH)₂ phase from excess Ni species weakening the crystallinity of the LDH structure though the content of Ni(OH)₂ is too less to be detected. Furthermore, it
- ⁵⁰ can be seen from Table S1 that the lattice parameter $c = 3d_{003}$ for all the precursors and supports is increased with Ni/Al ratios corresponding to gradual downshift of 2θ angles. One reason is the reduced layer charge density with increasing Ni content weakening the electrostatic attraction between the layer cations ⁵⁵ and the interlayer anions resulting in larger interlamellar spacing,
- another is the strong redox ability of Ni species makes laminates distorted.³⁶ The parameter $a (= 2d_{110})$ is also enhanced in the same order, implying the decrease of the arrangement density of

metal ions in brucite-like layers given the larger radii of Ni²⁺ 60 (0.72 Å) than Al³⁺ (0.50 Å) as the parameter *a* is a function of the mean radii of the layer metal cations. It is noted that the maximal Scherrer dimension for both precursors and supports occurs at x =3, implying the highest crystallinity of this system. The almost unaltered XRD peak positions and intensities for the precursors 65 compared with the supports indicates the well-kept LDH layer structure after loading of small amount of atomically precise Au₂₅Capt₁₈ clusters.

After calcination, it can be clearly seen from Fig. 2 that the Au₂₅/Ni_xAl-LDH (x=2, 3) catalysts possess definite lamellar ⁷⁰ structure though the (003) peaks shift to high 2θ angles due to the removal of interlayer water and partial CO₃²⁻ ions and the diffuse (110) and (113) peaks owing to the reduced orderliness of the layer cations. While for Au₂₅/Ni₄Al-LDH, the LDH laminate structure collapses upon the absence of the (001) lines and the 75 formation of mixed oxide phase indexed to cubic NiO highly dispersed in amorphous alumina matrix considering the broad weak (111), (200) and (220) peaks (JCPDS no. 471049). It is noticed that no XRD lines detected for Au phase implies the extremely small Au clusters on the catalysts. As for reference 80 catalyst Au₂₅/Ni(OH)₂, and extended systems Au₂₅/Ni_xMn-LDH (x = 2, 3), and Au₂₅/Ni_{3-x}Mn_xFe-LDH (x = 0.5, 0.8, 1) (Fig. S4), their XRD patterns show majorly collapsed LDH layers and obvious NiO phase though Au25/Ni2Mn-LDH and Au25/Ni2MnFe-LDH still maintain the weak (003) peaks.

The IR spectra (Fig. S5A) of the Au₂₅/Ni_xAl-LDH catalysts compared with the precursors and the supports mainly show the typical IR bands of the CO₃²⁻-LDH phase.¹³ The bands at 3489 cm⁻¹ of the precursor and support with Ni/Al ratio of 3 present as a narrower peak than the others, implying a more ordered cation ⁹⁰ distribution in the former,^{13,36} in line with its XRD data. Differently, beside the similar IR bands assigned to the LDH supports, the IR spectra of the Au₂₅Capt₁₈/Ni_xAl-LDH precursors show clear v_{C-H} mode of CH₃ and CH₂ groups of the captopril ligands, indicating the soft-land of Au₂₅Capt₁₈ clusters on the



Fig. 2 XRD patterns of the catalysts $Au_{25}/Ni_2Al-LDH$ (a), $Au_{25}/Ni_3Al-LDH$ (b), $Au_{25}/Ni_4Al-LDH$ (c) and the corresponding precursors $Au_{25}Capt_{18}/Ni_xAl-LDH$ (a', b', c') and supports $Ni_xAl-LDH$ (a_0, b_0, c_0).

LDH supports. However, the catalysts $Au_{25}/Ni_xAl-LDH$ (*x*=2, 3) only show the typical IR bands similar to corresponding precursors but greatly reduced v_{C-H} and clearly weak $v_{as}(COO^{-})$ (1553 cm⁻¹) and $v_s(COO^{-})$ (1332 cm⁻¹), implying the well-kept s LDH layer structure and the weak remains of the ligands. As for $Au_{25}/Ni_4Al-LDH$, absent v_{C-H} and very weak absorptions below

- A_{25}/M_4A_{1-LDH} , absent V_{C-H} and very weak absorptions below 1700 cm⁻¹ associated with CO₃²⁻ anions indicate the complete removal of the ligand and the partial preservation of the LDH layers, though XRD fails to detect the (003) line, leading to a ¹⁰ mixed oxides containing well-defined nickel oxide phase.^{36,37}
- Considering that the thiolate ligands may maintain the structural integrity of the Au₂₅Capt₁₈,²⁹ thus the structural integrity of Au₂₅ clusters in Au₂₅/Ni_xAl-LDH (x = 2, 3) are superior to that of Au₂₅/Ni₄Al-LDH. Partial remains of the ligands may also repress ¹⁵ the mobility of the Au₂₅ clusters beneficial to the monodisperse of the atomically precise Au₂₅ clusters on the LDH supports.

UV-vis/DR spectra show that all the samples (Fig. S5B) have similar optical absorption probably due to the major common LDH phases though Au₂₅/Ni₄Al-LDH shows very weak bands ²⁰ due to its poor layer structure. Two main absorptions around 380 and 650 nm with a respective shoulder at high wavelength are ascribed to the d-d spin-allowed electronic transitions of a Ni²⁺ ion in an octahedral field, due to the ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$ transition and ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ transition,^{36,38} respectively. However, ²⁵ there is no band at ~520 nm, typical for the localized surface plasmon resonance of Au NPs >2 nm,²¹ observed for both precursors and catalysts, implying the ultrafine Au clusters <2 nm existed in the Au₂₅/Ni_xAl-LDH cataysts. Among all the catalysts studied, Au₂₅/Ni₃Al-LDH shows the highest Ni²⁺ octahedral ³⁰ coordination symmetry, implying its best layer cations' order.

The N₂ adsorption-desorption analyses for all the catalysts and the supports (Fig. S6) show similar isotherms characteristics to each other. All the samples presents a Type IIb N₂ adsorption adsorption isotherm upon IUPAC classification, though their full ³⁵ adsorption-desorption isotherms show Type H3 hysteresis closing at ~0.4 (p/p^0) but Au₂₅/Ni₄Al-LDH at ~0.25 (p/p^0) associated with the aggregates of the plate-like particles resulting in slit-shaped mesopores.^{36,39} The pore size distributions reveal a series of nonuniform mesopores from 2 to 50 nm. The BET areas (S_{BET}) of the ⁴⁰ catalysts Au₂₅/Ni₄Al-LDH with x=2, 3, and 4 as 127, 108, and 181 m²/g, respectively, are larger than corresponding supports (113, 105, 126 m²/g) because the interlayer anions and water molecules are deprived partially upon calcination leading to the formation of mesoporous. The increment of S_{BET} of the catalysts

⁴⁵ compared to supports reduce in an order of Au₂₅/Ni₄Al-LDH (54.9 m²/g) < Au₂₅/Ni₂Al-LDH (14.3 m²/g) < Au₂₅/Ni₃Al-LDH (2.2 m²/g), in line with the destruction degree of LDH layers, *i.e.*, Au₂₅/Ni₃Al-LDH maintains the highest layer structure orderliness.

- The SEM images of all the samples (Fig. S7) indicate that the $_{50}$ Ni_xAl-LDH supports have clear platelet-like morphology with an even surface and the crystallite size in the *ab*-direction is *ca*. 20-40 nm. As shown in Fig. S7(a',b',c'), the morphology of the catalyst precursors is analogous to those of the supports, suggesting the adsorption of Au₂₅ clusters onto the supports has
- ⁵⁵ little effects on the features of the supports, in line with the XRD and IR data. Then, the Au₂₅/Ni_xAl-LDH catalysts (Fig. S7(a,b,c)) show the similar platelet-like morphology for Au₂₅/Ni₂Al-LDH and Au₂₅/Ni₃Al-LDH especially the latter with well-kept

regularity and smooth surface in spite of a little aggregation, ⁶⁰ while Au₂₅/Ni₄Al-LDH shows serious aggregation, irregular plate shape and rough surface probably maybe due to its collapsed LDH layer along with NiO phase doped.

The SEM-mapping of Au₂₅/Ni_xAl-LDH (Fig. S8) indicates that the elements Ni, Al and Au are uniformly dispersed in the ⁶⁵ catalyst samples. Moreover, the edge sites of LDH nanoplates may predominantly draw Au₂₅ clusters due to the exposure of more unsaturated dangling M-OH groups with high potential for smaller hexagonal LDH nanoplates (20-40 nm) than the larger ones (~50-80 nm) reported previously.³¹

The HRTEM images of the Au₂₅/Ni_xAl-LDH catalysts (Fig. 3) clearly show that the ultrafine Au₂₅ clusters are highly dispersed on the edge sites of the hexagonal LDH platy particles, probably due to the more pending M-OH functional groups near the edge sites of the supports. The Au₂₅/Ni₂Al-LDH and Au₂₅/Ni₃Al-LDH ⁷⁵ present approximately atomic precise Au clusters of 0.9 ± 0.3 nm and 0.9 ± 0.2 nm, almost same as the pure Au₂₅Capt₁₈, respectively, implying the existence of strong metal-support interaction between Au₂₅ clusters and Ni_xAl-LDH (x = 2, 3) supports which have the better layer structure even after 300 °C

⁸⁰ calcination. While Au₂₅/Ni₄Al-LDH has Au cluster size of 1.1 ± 0.4 nm, slightly larger than the pure Au₂₅Capt₁₈, indicating the less strong Au₂₅-LDH interaction for this sample with largely collapsed LDH layers structure along with partial NiO doped thus Au₂₅ clusters are easy to migrate during the calcination leading to

- ss slight increase of Au cluster size. Furthermore, the highmagnified HRTEM images (insets in Fig. 3) show that all the catalysts exhibit both the nanocrystalline Au with (111) lattice fringes (0.235 nm) and the LDH with (015) lattice fringes (0.225 nm). These two lattice fringes for $Au_{25}/Ni_xAl-LDH$ (x = 2, 3) are
- 90 nearly parallel to each other, implying the possible epitaxial growth of Au₂₅ clusters on the LDH supports favoring the ultrafine Au₂₅ cluster sizes and the strong gold-LDH synergy upon the epitaxial diffusion of Au₂₅ clusters onto the LDH surface. While these two lattice fringes for Au₂₅/Ni₄Al-LDH are 95 not parallel to each other but have certain angle of the cross, probably due to the lower match between the Au₂₅ clusters and the support owing to the collapsed LDH layer with the incorporated NiO phase leading to the slightly aggregated Au₂₅ clusters. The FFT images of Au₂₅/Ni_xAl-LDH (x = 2, 3) further 100 depict the brighter diffraction dots for LDH phase than for Au₂₅ nanoclusters, just contrary to those of Au₂₅/Ni₄Al-LDH, also demonstrating the better kept LDH layer of the former and even smaller Au₂₅ sizes than the latter, which may strengthen the synergestic effect between the Au₂₅ clusters and the LDH thus in 105 favor of the alcohol oxditaion reaction.

Fig. 4 shows typical HAADF-STEM image of $Au_{25}/Ni_3Al-LDH$ and size distribution for Au_{25} clusters upon *ca*. 100 clusters. The comparison of Au content in EDX spectra (Fig. S9) confirms that the bright spots in Fig. 4A are indeed Au_{25} clusters. The average diameter of the Au_{25} clusters in $Au_{25}/Ni_3Al-LDH$ appeares to be 0.9 ± 0.2 nm, comparable to that of the pristine $Au_{25}Capt_{18}$ cluster, indicating the well-preserved sizes of the Au_{25} clusters during the calcination. Close inspection of Fig. 4A reveals that the monodispersed Au_{25} clusters are distributed ¹¹⁵ mostly at the edge of the LDH nanoplates, in line with the HRTEM result.



Fig. 3 HRTEM images of Au_25/Ni_2Al-LDH (a), Au_25/Ni_3Al-LDH (b) and Au_25/Ni_4Al-LDH (c).





Table 1 shows the catalytic activities of the catalysts in 10 oxidation of 1-phenylethanol to acetophenone with molecular oxygen as a sole oxidant at atmospheric pressure under base-free conditions. Initially, the catalysts were evaluated at 60, 70, 80, 90 and 100 °C in toluene. Pristine Ni_xAl-LDH supports display verylow conversion of 1-phenylethanol (<4%), indicating that 15 Au₂₅ clusters are the active species for the aerobic alcohol oxidation reaction as previously reported.19,40,41 The pure Au₂₅Capt₁₈ clusters also fail to show any activity could be attributed to the existence of the ligands which significantly inhibit the access of reactants to the Au25 clusters' surfaces. It can 20 be clearly seen that in terms of the same catalyst, the conversion and TOF of 1-phenylethanol oxidation increase with the reaction temperatures. At 80 °C, the TOF values increase in an order of $Au_{25}/Ni_{4}Al-LDH$ (4960 h⁻¹) < $Au_{25}/Ni_{2}Al-LDH$ (5310 h⁻¹) < Au₂₅/Ni₃Al-LDH (5870 h⁻¹). The Au₂₅/Ni₃Al-LDH exhibits the 25 highest TOF value. Specially using a little higher catalyst loading, exactly same conditions as our previous work, ³¹ Au₂₅/Ni₃Al-LDH gives the TOF of 6607 h⁻¹, which is ca. 16.2% better than in the formerly published 5687 h⁻¹ on AuNCS/Ni₃Al-LDH-0.22 (AuNCs: ~1.5 nm)³⁰ and dramatically higher than 1101 h⁻¹ over 30 Au/2Ni-Al (AuNP: 4.5 nm) which employed about five times lower amount of substrate, five times higher catalyst loading and four times higher amount of toluene at 100 °C in Zhao's report.²⁰ Also, the Au₂₅/Ni₃Al-LDH catalyst gives the conversion of 10.2% of the oxidation of 1-phenylethanol in the absence of O_2 .

35 Moreover, besides similar dependence in activity-temperature (120, 130, 140, 150 and 160 °C) and activity-catalyst composition (x = 2, 3, 4) to those in toluene, the Au₂₅/Ni_xAl-LDH catalysts clearly exhibit extraordinarily high activity in the solvent-free oxidation of 1-phenylethanol (Table 1). The TOF at 160 °C of 40 118500 h⁻¹ with 23.7% yield of acetophenone is achieved for Au₂₅/Ni₃Al-LDH, which is much better than those of the previously reported Au/PI (20000 h⁻¹)⁸, Au/MgAl-HT (37000 h⁻¹)⁸ 1)42, AuNCs/Ni₃Al-LDH-0.22 (46500 h⁻¹)31, and Au/Mg₃Cr-HT (81000 h⁻¹)¹⁹ under similar catalytic reaction conditions. These 45 results unequivocally demonstrate the significant increase in aerobic oxidation activity for alcohols by nearly atomic precise monodispersed Au₂₅/Ni_xAl-LDH catalysts. Importantly, the Au₂₅/Ni₃Al-LDH catalyst with ultrafine Au₂₅ clusters (~0.9 nm) and well-kept LDH layer structure presents the highest activity. 50 Similar regularity is also found in the Au₂₅/Ni_xMn-LDH and Au₂₅/Ni_{3-v}Mn_vFe-LDH systems for aerobic oxidation of 1phenylethanol. The TOF of 4070 h⁻¹ for Au₂₅/Ni₂Mn-LDH with better LDH layer structures is obviously higher than that of

View Article Online	8	of	15
DOI: 10.1039/C6CY00186F	Č	0	

Catalyst	Au/wt % ^[b]	T ∕°C	Conv. /%	Sel. /%	TOF /h ⁻¹ [c]
Au ₂₅ /Ni ₂ Al-LDH	0.197	60	45.3	99	4530
		70	50.1	99	5010
		80	53.1	99	5310
		90	57.2	99	5720
		100	61.9	99	6190
Au ₂₅ /Ni ₃ Al-LDH	0.191	60	51.8	99	5180
		70	55.4	99	5540
		80	58.7	99	5870
		80	99.1	99	6607 ^[d]
		90	63.8	99	6380
		100	67.8	99	6780
		100	10.2	99	1020 ^[e]
Au ₂₅ /Ni ₄ Al-LDH	0.195	60	32.0	99	3200
		70	40.1	99	4010
		80	49.6	99	4960
		90	52.5	99	5250
		100	55.5	99	5550
Au ₂₅ /Ni ₂ Al-LDH ^[f]	0.197	160	19.5	99	97500
Au ₂₅ /Ni ₃ Al-LDH [f]	0.191	160	23.7	99	118500
Au ₂₅ /Ni ₄ Al-LDH [f]	0.195	160	14.2	99	71000
Au ₂₅ /Ni(OH) ₂	0.203	80	21.8	99	2180
Au ₂₅ /Ni ₂ Mn-LDH	0.201	80	40.7	99	4070
Au ₂₅ /Ni ₃ Mn-LDH	0.198	80	37.1	99	3710
Au25/Ni2MnFe-LDH	0.191	80	34.1	99	3410
$Au_{25}/Ni_{2.2}Mn_{0.8}Fe\text{-LDH}$	0.185	80	31.6	99	3160
Au25/Ni25Mn05Fe-LDH	0.179	80	27.8	99	2780

^[a] 1-phenylethanol (5 mmol), catalyst (Au: 0.01 mol%), toluene (5 mL), O₂ bubbling (20 mL/min), 1 h. ^[b] Based on ICP. ^[c] Moles of alcohol converted per mole of Au per hour. ^[d] 1-phenylethanol (10 mmol), catalyst (Au: 0.015 5 mol%), toluene (10 mL), O₂(20 mL/min), 1 h, same as in ref 31. ^[e] 1-phenyl-

- ethanol (5 mmol), catalyst (Au: 0.01 mol%), toluene (5 mL), preevacution by Ar for 1 h before heating to reaction Temp., all in Ar (8 mL/min). ^[f] 1-phenyl-ethanol (100 mmol), catalyst (Au: 4.0×10^{-4} mol%), O₂ (20 mL/min), 30 min.
- ¹⁰ Au₂₅/Ni₃Mn-LDH (3710 h⁻¹) with collapsed LDH layers though both show lower TOF values than those of Au₂₅/Ni_xAl-LDH catalysts. These observations imply that the layer structure of the LDH supports may play important role on the alcohol oxidation, regardless of their varied specific surface areas just as that the ¹⁵ Au₂₅/Ni₄Al-LDH with collapsed LDH layers possesses poor
- alcohol oxidation activity despite of its larger S_{BET} (181 m²/g) than Au₂₅/Ni₃Al-LDH (108 m²/g).

The unprecedentedly high aerobic oxidation activity of Au₂₅/Ni₃Al-LDH for 1-phenylethanol may be not only ascribed to ²⁰ the nearly atomic precise Au₂₅ clusters and higher LDH layer regularity, but also to the strongest Au₂₅-LDH interaction. The

- reason comes from three aspects. 1) The modified electrostatic adsorption strategy upon LDH-predispersed buffer for highly efficient electrostatic adsorption of the negatively charged
- ²⁵ Au₂₅Capt₁₈ clusters as near monodispersion over the edge sites of the hexagonal LDH nanoplates, compared to the simple impregnation-adsorption by directly adding LDH powders into

the Au clusters' solution.³¹ 2) The deposition of atomically precise Au₂₅ clusters may provide more favourable Au₂₅ surface ³⁰ electronic state thus a highly active Au clusters catalyst probably through a beneficial modification for the electronic structure of the Au core. 3) The proper layer charge density of the supports such as 0.25 for Ni₃Al-LDH may be beneficial to the mono-dispersion of Au₂₅ clusters onto the edge sites of LDH support ³⁵ thus strengthen the Au₂₅-LDH synergy, compared with the LDH supported non-atomically precise Au nanoclusters catalysts.³¹

After reaction, the Au₂₅/Ni₃Al-LDH catalyst was filtered out, washed with solvent for another five recycles. The activities of 1phenylethanol oxidation were well-kept in all the recycles. The ⁴⁰ ICP data for reaction mixture show no Au species detected, implying the strong interaction between Au₂₅ clusters and LDH support. In addition, after filtering out the catalyst, no further conversion of 1-phenylethanol was observed, indicating that the catalyst was heterogeneous in nature. The recovered catalyst after ⁴⁵ five runs were also characterized by HRTEM (Fig. S10), which shows almost same morphology as the fresh one, indicating the high structural stability of the present catalyst.

Furthermore, Au/Ni₃Al-LDH could also selectively oxidise a variety of alcohols to corresponding carbonyl compounds with 50 high activity, indicating a high versatility of the nearly atomic precise Au₂₅/Ni_xAl-LDH catalyst. The Au₂₅/Ni₃Al-LDH exhibits comparable or higher activities not only for benzylic secondary alcohols including 1-phenylethanol and benzhydrol (Table 2, entries 1 and 5), but also for aliphatic secondary alcohols such as 55 cyclohexanol (Table 2, entry 9), compared with Au/HT catalysts previously reported (Table 2, entries 2-4, 6-8 and 10-12) at high conversion.^{20,31,42} Meanwhile, Au₂₅/Ni₃Al-LDH presents higher activity of benzylic primary alcohols oxidation (Table 2, entry 13), compared with literature values (Table 2, entries 14, 15 and 60 16).^{19,20,31} We also note that Au₂₅/Ni₃Al-LDH displays higher activity for the selective oxidation of allylic alcohols, for example, cinnamyl alcohol can be selectively oxidized to cinnamyl aldehyde with 93.3% yield in 4 h (Table 2, entry 17). Moreover, it should be noted that for all these alcohols oxidation activity 65 data, the amount of the Au₂₅/Ni₃Al-LDH catalyst employed in the reaction is almost 2 times less than that of Au/2Ni-Al beside 4 times lower amount of toluene used,²⁰ implying the excellent catalytic activity of the present nearly atomic precise Au₂₅/Ni₃Al-LDH catalyst upon the modified electrostatic adsorption method. 70 All these results indicate that the Au₂₅/Ni_xAl-LDH catalysts are highly effective for the aerobic oxidation of alcohols.

To reveal the natural reason for different alcohols oxidation performance of the series of Au₂₅/Ni_xAl-LDH catalysts, we study the macroscopic kinetic process of the catalysts, containing the 75 effect of the Ni/Al molar ratios and reaction temperatures on the reaction rate for the aerobic oxidation of 1-phenylethanol. Timeevolution of conversion, *C*, was monitored from the measured yield of product as show in Fig. S11. It can be seen that the timeconversion plots are linear up to approximately 60% conversion 80 of 1-phenylethanol in all the reactions in toluene (Fig. S11(A)), implying that the product inhibition is very small. As shown in Fig. 5 (in toluene) and Fig. S12 (solvent-free), the term -ln(1-*C*) is increased linearly with the reaction time (h) for all Au₂₅/Ni_xAl-LDH catalysts, indicating that the reaction is first order with 85 respect to 1-phenylethanol. The rate constant, *k*, was therefore

obtained from the slope of the $-\ln(1-C)$ plot as a function of reaction time. The rate constant *k* values for 1-phenylethanol oxidation at 60-100 °C in toluene (Table S2) are larger than those at 120-160 °C without solvent (Table S3). The *k* values of 1-⁵ phenylethanol oxidation with and without solvent at the same temperature are increased in an order of $Au_{25}/Ni_4Al-LDH < Au_{25}/Ni_2Al-LDH < Au_{25}/Ni_3Al-LDH$.

A good linear correlation is obtained by plotting of $\ln k$ versus the inverse of the temperature, and apparent ¹⁰ activation energy, $E_{\rm a}$, could be estimated with the slope. The least-square fit analysis yields E_a values of 15.31 kJ/mol for the optimal catalyst Au₂₅/Ni₃Al-LDH and 17.91 kJ/mol for Au₂₅/Ni₂Al-LDH, respectively, both smaller than the 21.62 kJ/mol for Au₂₅/Ni₄Al-LDH in toluene (Fig. 5). Meanwhile, 15 the E_a values for 1-phenylethanol oxidation under solventfree conditions are 19.01, 16.9 and 22.56 kJ/mol, respectively, for Au₂₅/Ni_xAl-LDH samples with x = 2, 3, and 4 (Fig. S12). The E_a values of all the Au₂₅/Ni_xAl-LDH catalysts for 1-phenylethanol oxidation reaction in toluene 20 are lower than corresponding ones obtained in solvent-free reactions, and the E_a values of 1-phenylethanol oxidation with and without solvent are decreased in an order of $Au_{25}/Ni_4Al-LDH > Au_{25}/Ni_2Al-LDH > Au_{25}/Ni_3Al-LDH.$ The highest k and the lowest E_a values of Au₂₅/Ni₃Al-LDH 25 imply its optimal electronic structure and strong metalsupport interaction between the ultrafine Au clusters with nearly atomic precise and the Ni₃Al-LDH support with the highest layer regularity.

The XPS analysis was used to explore the effect of the ³⁰ electronic structure of the Au₂₅/Ni_xAl-LDH catalysts on the catalytic activity (Fig. 6). The Au 4f_{7/2} binding energy (BE) of Au₂₅Capt₁₈ located at 84.7 eV exhibits a ~0.7 eV shift to the higher BE compared to the bulk gold (84.0 eV) owing to the electron donation from Au₂₅ to the surface thiolates,²¹ ³⁵ approving the formation of Au-S bond for the Au₂₅Capt₁₈ cluster. The Au₂₅/Ni_xAl-LDH (x = 2, 3, 4) catalysts exhibit the Au 4f_{7/2} BE at 83.42, 83.34 and 83.52 eV, respectively, clearly smaller than 84.0 eV of the bulk gold, ascribed to the lower coordination number of surface Au atoms of ultrafine ⁴⁰ Au₂₅ cluster (< 2 nm), indicating that the Au₂₅ clusters on the catalysts are negatively charged^{7,41,43} and there exists an electron transfer from Ni_xAl-LDH to the surface of the Au₂₅

- clusters. The reason for electron transfer from LDH supports to Au₂₅ clusters can be explained as follows. Given that ⁴⁵ electron affinity of neutral gold particle is size-dependent,⁴² as the size is remarkably reduced to less than ~5 nm, surface Au atoms on the nanoparticles behave more like a single Au
- atom, are highly active and easily anionically ionized. Considering the electron affinity of a single Au atom of 2.3 ⁵⁰ eV,⁴⁴ larger than the threshold value of electron transfer, the driving force for electron transfer from the LDH surface to
- Au atoms originates from surface conjugation and the differential Fermi energy level, and it takes some charge to equalize the Fermi levels.^{44,45} In detail, the Au $4f_{7/2}$ BE ⁵⁵ values of Au₂₅/Ni_xAl-LDH (x = 2, 3, 4) catalysts show 0.58,
- ⁵⁵ Values of Au₂₅/Ni_xAl-LDH (x = 2, 3, 4) catalysts snow 0.58, 0.66 and 0.48 eV downshift from the bulk Au, respectively, indicating that the amount of electrons transferred from LDH to Au₂₅ clusters increases in an order of Au₂₅/Ni₄Al-LDH <

 $\label{eq:composition} \begin{array}{l} \mbox{Table 2} \mbox{ Aerobic oxidation of various alcohols to corresponding carbonyl} \\ {}_{60} \mbox{ compounds over } \mbox{Au}_{25} / \mbox{Ni}_3 \mbox{Al-LDH}.^{[a]} \end{array}$

Entry	Substrate	Au/substrate	Conv.	Sel.	Time
		[mol %]	[%]	[%]	[h]
1	ОН	0.115	99.9	99	0.25
2 ^[b]	\sim	0.115	99.9	99	0.5
3 ^[c]		0.45	99	99	0.33
4 ^[e]		0.25	>99	>99	4
5	\land	0.115	99.9	99	3
6 ^[b]		0.115	99.9	99	4
7 ^[c]	\sim γ \sim	0.45	99	96	4
8 ^[e]	он	0.25	99	>99	4
9		0.115	99.2	99	4
$10^{[b]}$	🗸 🗡 он	0.115	98.3	99	4
11 ^[c]		0.45	93	97.8	4
12 ^[e]		0.25	11	>99	4
13	ОН	0.115	99.5	99	0.5
14 ^[b]		0.115	95.3	99	2
15 ^[d]	\checkmark	0.2	96	>99	1
16 ^[e]		0.25	57	>99	2
17	ОН	0.115	93.3	95	4
18 ^[b]		0.115	77.0	96	4
19 ^[e]	\sim	0.25	54	99	2

^[a] Alcohols (1 mmol), Au₂₅/Ni₃Al-LDH (Au: 0.115 mol%), toluene (5 mL), 80 °C, O₂ bubbling (20 mL/min). ^[b] Alcohols (1 mmol), AuNCs/Mg₃Al-LDH-0.23 (Au: 0.115 mol%), toluene (5 mL), 80 °C, O₂ bubbling (20 mL/min) in ref 30. ^[c] Alcohols (1 mmol), Au/HT (0.1 g, 0.45 mol%),
⁶⁵ toluene (5 mL), 80 °C, air (1 atm) in ref 42. ^[d] Alcohols (1 mmol), Au/MgCr-HT (Au: 0.2 mol%), toluene (10 mL), 100 °C, O₂ bubbling (20 mL/min) in ref 19. ^[e] Alcohols (1 mmol), Au/2Ni-Al (0.05 g, Au 1 wt%), toluene (20 mL), mole ratio of alcohol/Au=400, 80 °C, O₂ bubbling (15 mL/min) in ref 41.

⁷⁰ Au₂₅/Ni₂Al-LDH < Au₂₅/Ni₃Al-LDH. This trend is in accordance with the activity results, just as Tsukuda *et al.*⁷ reported that the catalytic activity of Au NPs for aerobic oxidations is enhanced by an increase in the amount of negative charge on the Au core, therefore further suggesting ⁷⁵ that the interaction between the Au₂₅ clusters and the LDH supports increases in an order of Au₂₅/Ni₄Al-LDH < Au₂₅/Ni₂Al-LDH < Au₂₅/Ni₃Al-LDH.

In order to get more insight into the surface characteristics of the catalysts, Ni 2p and O 1s spectra were carefully analysed for the catalysts and pristine supports (Fig. S13, Fig. S14, and Table S4). The Ni 2p_{3/2} BE values of Ni_xAl-LDH shift to lower values with increasing Ni/Al ratios because the amount of positively charged AlO₆ octahedra partially substituted neutral NiO₆ octahedra in the layer become less and the electron cloud density surrounding the nickel nuclei increase.^{13,20} As for the Au₂₅/Ni_xAl-LDH catalysts, the peaks at ~856 and ~862 eV are assigned to the spin-orbit spilt lines and shake-up satellite of Ni 2p_{3/2},⁴⁶ higher than those of corresponding Ni_xAl-LDH supports, indicating that there are a strong interaction between supports and Au₂₅ clusters on and probably a electron transfer from Ni-OH octahedra to Au₂₅ clusters through the interaction of Au-O(H)-Ni, in conformity

with the Au 4f XPS data.



Fig. 5 -ln(1-*C*) against time and Arrhenius plots for the aerobic oxidation of 1-phenylethanol catalyzed by Au_{25}/Ni_xAl -LDH (x = 2, 3, 4) at different reaction temperatures. Reaction conditions: 1-phenylethanol (5 mmol), 5 catalyst (Au: 0.01 mol%), toluene (5 mL), O₂ (20 mL/min).



Fig. 6 Au 4f XPS spectra of Au_{25}/Ni_2Al -LDH (a), Au_{25}/Ni_3Al -LDH (b), Au_{25}/Ni_4Al -LDH (c) and $Au_{25}Capt_{18}$.

The curve fitting of O 1s spectra of Ni_xAl-LDH and ¹⁰ Au₂₅/Ni_xAl-LDH reveals that there are two oxygen species including surface OH groups and lattice O²⁻ species. The amount of surface OH groups of Ni_xAl-LDH increases with increasing Ni/Al ratios. The curve fitting of O 1s spectrum of Au₂₅/Ni₂Al-LDH reveals that surface OH (52.40%) is 4.99% lower than those

- ¹⁵ of Ni₂Al-LDH (57.39%) and the surface OH of Au₂₅/Ni₃Al-LDH (60.52%) is 4.16% lower than that of Ni₃Al-LDH (64.68%), while for Au₂₅/Ni₄Al-LDH, the surface OH (46.56%) is 22.77% lower than that of Ni₄Al-LDH (69.33%). Dai *et al.*⁴³ studied the interaction between the Au clusters and a Mg(OH)₂'s basal plane
- ²⁰ by using a DFT theory, and found strong interaction of the Au clusters with the surface –OH groups *via* a short bond between edge Au atoms and O atoms of the hydroxyls helping the Au clusters against sintering and stabilizing Au clusters *via* Au-OH linkage thus contributing to the CO-oxidation activity. The
- ²⁵ amount of surface –OH groups of Au₂₅/Ni_xAl-LDH is consistent with the order of alcohol oxidation activities, indicating that the – OH function groups on Au₂₅/Ni_xAl-LDH is advantageous to the activation of substrate alcohols and further results in the

improvement of reactivity. Moreover, the charge density of the ³⁰ LDH layer, regarding the reactivity, is affected by the orderliness of the layer cations. The well ordered arrangement of cations on the LDH layer surfaces, corresponding to the uniform distribution of the charge density⁴⁷, directly causes the maximal synergistic effect between the Au₂₅ clusters and the Ni₃Al-LDH.

- It should be mentioned that the recovered Au₂₅/Ni₃Al-LDH catalyst after five runs were also characterized by XPS (Fig. S15), which shows almost same surafce Au oxide state as the fresh one, supporting the high recyclability of the present nearly atomic precise Au₂₅/Ni₃Al-LDH nanocatalyst.
- The electronic state of Au₂₅ clusters and the surface acidity of the Au₂₅/Ni_xAl-LDH catalysts were further studied by CO adsorption in combination with IR spectra (Fig. 7). In order to discriminate between the adsorption properties of the surface Au atoms and the supports, CO adsorption was first studied on pure 45 supports. The Ni_xAl-LDH supports did not show any pronounced IR bands in 2000-2100 cm⁻¹ when exposed to a CO flow. Only prominent broad band occurred at ca. 2170 cm⁻¹ can be assigned to the stretching mode of CO adsorbed on Brønsted acid sites associated to AlO-H $^{\delta+}$ centres.^{18,48} The fact that the LDH and 50 LDH-derived mixed oxides hold both strong acidity and basicity have ever been reported by Wang et al.¹⁸ and Corma's group.⁴⁸ It is believed that CO molecules are adsorbed atop of Au atoms of clusters and surfaces, thus, the stretching frequency (v_{CO}) of adsorbed CO mainly reflects the electron density on the $_{55}$ adsorption sites, and the v_{CO} is red- and blue-shifted compared with that of free CO as CO is adsorbed on anionic and cationic Au sites, respectively.49-52 In our cases of Au₂₅/Ni_xAl-LDH catalysts, besides the bands at ~2170 cm⁻¹ due to the CO adsorbed on supports, prominent IR bands at 2102, 2097 and 2108 cm⁻¹ for 60 Au₂₅/Ni₂Al-LDH, Au₂₅/Ni₃Al-LDH and Au₂₅/Ni₄Al-LDH,
- respectively, exhibit prominent red-shift, compared to literature values in 2110-2125 cm⁻¹ upon Au⁰ carbonyls of Au NPs^{7,53-55}, attributing to the greater π back-donation from the negatively charged Au₂₅ clusters. Also, all the bands marked by arrows in ⁶⁵ Fig. 7 with an asymmetric broadening from the low-frequency side are clearly observed, which can be assigned to CO adsorbed on Au₂₅ clusters and the low frequency broadening may be associated with the CO adsorbed on sites at the perimeter of Au clusters of the catalysts considering their absence in the supports ⁷⁰ and the similarity to previous reports.^{48,56,57}

It is worth mentioning that the obviously observed IR bands of Au₂₅/Ni_xAl-LDH at 50 °C slowly decay during N₂ evacuation within 30 min, rather analogous to the observations of the CO adsorbed on the Au cores of Au:PVP (~1.3 nm) in CH₂Cl₂ at 295 ⁷⁵ K in purging argon previously reported by Tsukuda et al.⁷, probably owing to the similar ultrafine Au core in the present catalysts to Au:PVP system. The ν_{CO} value for both Au_{25}/Ni_2Al-LDH and Au₂₅/Ni₃Al-LDH is greatly red-shifted from that of Au₂₅/Ni₄Al-LDH, implying more negatively charged Au clusters 80 on the former two samples. As compared with the red-shifted values, we can know that the amount of negative charge of Au₂₅ clusters on the Au25/NixAl-LDH catalysts increases in an order of $Au_{25}/Ni_4Al-LDH < Au_{25}/Ni_2Al-LDH < Au_{25}/Ni_3Al-LDH$ consistent with the XPS analysis and alcohol oxidation activities, 85 suggesting the more negatively charged Au₂₅ clusters on the catalysts is more favourable for the oxidation of alcohols.



Fig. 7 CO adsorption FT-IR spectra of Au_{25}/Ni_2Al -LDH (a), Au_{25}/Ni_3Al -LDH (b), Au_{25}/Ni_4Al -LDH (c), Ni_2Al -LDH (a₀), Ni_3Al -LDH (b₀), and Ni_4Al -LDH (c₀).



Fig. 8 TPSR diagram of isopropanol on $Au_{25}/Ni_2Al-LDH$ (a), $Au_{25}/Ni_3Al-LDH$ (b), $Au_{25}/Ni_4Al-LDH$ (c), $Ni_2Al-LDH$ (a), $Ni_3Al-LDH$ (b), and $Ni_4Al-LDH$ (c).

To obtain more insights into the gold-support interactions, we 10 compared the TPSR of pre-adsorbed isopropanol on Au₂₅/Ni_xAl-LDH catalysts and Ni_vAl-LDH supports. Generally, isopropanol will undergo dehydrogenation over basic sites to form acetone and H₂ and dehydration over acid sites to yield ethylene and $H_2O^{.58}$ The evolution of H_2 for $Au_{25}/Ni_xAl-LDH$ catalysts is 15 shown in Fig. 8. Clearly, quite weak H₂ signals could be detected for all the three LDH supports, quite similar to Liu's report,¹⁹ indicating the quite weak dehydrogenation abilities of the pure LDH supports, in conformity with their undetected alcohol oxidation activities. However, exceptionally strong H₂ signals for 20 Au₂₅/Ni_rAl-LDH catalysts can be achieved at much lower temperatures compared to corresponding LDH supports. The gaps of the desorption temperatures between the catalysts and the supports are in an increasing order of Au₂₅/Ni₄Al-LDH (13 °C) < Au₂₅/Ni₂Al-LDH (27 °C) < Au₂₅/Ni₃Al-LDH (33 °C), suggesting

- ²⁵ that all the Au₂₅/Ni_xAl-LDH catalysts have much higher dehydrogenation activity compared with pristine supports. This trend is just in accordance with the order of alcohol oxidation activity, indicating the gradually increasing Au₂₅-LDH synergetic interactions in Au₂₅/Ni_xAl-LDH catalysts, as the above XPS ³⁰ shows. These results indicate that the loading of Au₂₅ onto the
- surface of the LDH support significantly facilitate the

dehydrogenation process of the adsorbed isopropanol, that means, the Au₂₅/Ni_xAl-LDH catalysts have excellent dehydrogenation abilities especially Au₂₅/Ni₃Al-LDH showing the highest rate for ³⁵ oxidation of alcohols due to its strongest Au-LDH synergetic effect associated with both the ultrafine nearly atomic precise Au₂₅ clusters and the well-kept Ni₃Al-LDH layer structure.

The present results implies that the strong Au₂₅-LDH interactions featured as the critical effect on the electronic ⁴⁰ structure of the Au₂₅ clusters play key roles on the various aerobic alcohol oxidation activity of the Au₂₅/Ni_xAl-LDH catalysts. Meanwhile, unprecedentedly higher oxidation activity of Au₂₅/Ni₃Al-LDH than most previously reported catalysts may also be benefited from the existence of Brønsted basic sites (M-⁴⁵ OH^{δ-}) on the catalyst for the initial O-H bond cleavage, as most reports previously pointed, ^{19,40-42} as well as the existence of surface nickel sites and Au₂₅ clusters for improving the cleavage of C-H bond to create the carbonyl compound. The existence of Brønsted acid sites on the surface of the catalysts may also facilitate the alcohol oxidation process as Wang *et al.* reported.¹⁸ Based on the above analysis, the nature of the active sites of the Au₂₅/Ni_xAl-LDH catalysts are illustrated in Scheme 2.

From the above results, the following correlations between the electronic structures and the oxidation activity of the 55 Au₂₅/Ni_xAl-LDH catalysts can be summarized. (1) Smaller Au clusters (Au₂₅/Ni_xAl-LDH (x = 2, 3) that can donate more electronic charge to CO molecules exhibit higher activity toward aerobic oxidation than the larger Au clusters (Au₂₅/Ni₄Al-LDH). (2) When the Ni/Al molar ratio increases from 2 to 4, the areas of 60 coordination sites for CO molecules are obviously reduced as shown in Fig. 7. Contrary to expectations from decrease in the area available for catalysis, the activity of Au₂₅/Ni₃Al-LDH reaches the highest. This result can be explained in that the decrease of the cluster surface area available for catalysis is 65 compensated by the enhancement of activity per unit surface area by the donation of more electronic charge from the LDH support. (3) The charge state of Au₂₅ clusters supported on Ni₃Al-LDH is more negative than that by Au₂₅/Ni₂Al-LDH, and the activity for oxidation is much higher than that of Au₂₅/Ni₂Al-LDH, despite 70 their comparable core sizes (Fig. 3). This implies that the higher reactivity of the former is due to the higher electron-donating ability of Ni₃Al-LDH, although the possibility that the surface areas available for catalysis are smaller for Au₂₅/Ni₃Al-LDH than for Au25/Ni2Al-LDH is not totally excluded. All of these 75 correlations indicate that the catalytic activity of small (<1.5 nm) Au₂₅ clusters for aerobic oxidation is enhanced by an increase of negative charge on the Au core. This may provide an empirical rule for the fabrication of supported active Au catalysts; more electronic charge could be deposited into high-lying orbits of 80 ultrafine Au₂₅ clusters by doping with electropositive elements such as Pd²⁴ or by interaction with nucleophilic sites of stable supports.

Tsukuda *et al.*^{7,26,59} studied the effect of electronic structures of Au clusters on aerobic alcohol oxidation, and demonstrated st hat cleavage of the C-H bond at the benzylic position is the ratedetermining step upon kinetic isotope effect. Particularly, Tsukuda *et al.*⁷ have ever reported the anionic Au cores of Au:PVP on the electron donotation from PVP in aerobic oxidation of *p*-hydroxybenzyl alcohol with K₂CO₃ additive, and



Scheme 2 The nature of the active sites of the Au₂₅/Ni_xAl-LDH catalysts.

- proposed that an extra electron from the gold readily transfers to ⁵ the LUMO (π^*) of adsorbed O₂, based on similar observations of Au cluster anions *via* gas-phase studies,^{49,60} which weakens the O-O bond and activates oxygen molecule to form superoxo- or peroxo-like species for further catalytic reaction, which may play an essential role in the alcohol oxidation. In the present work, the ¹⁰ lower activation energy E_a for aerobic oxidation of 1-phenylethanol over Au₂₅/Ni₃Al-LDH compared to other samples clearly indicates the greatly promoted synergy between Au₂₅ and Ni-OH groups from the higher LDH layer regularity. It is shown that the catalytic activity is enhanced with increasing electron density on ¹⁵ the Au core.
- Generally, the aerobic oxidation of alcohols catalyzed by LDH-loaded Au catalysts may involve the assumption that the rate-determining step, the β -H elimination of a metal alkoxide intermediate on the heterogeneous metal surface, is ²⁰ the same on metal oxides loaded noble metal catalysts, ^{9,61} and uniquely, the basic sites on the LDH supports activate the O-H bond of the alcohols to promote the formation of the metal alkoxide. ^{17,19,41} The activation of oxygen by supported metals⁶² or surface oxygen vacancies of the supports⁶¹ is ²⁵ another critical step for formation of water. Thus upon all the above experimental and characteristic results and the previous findings^{20,42,62}, we tentatively propose a possible aerobic oxidation mechanism for alcohols on Au₂₅/Ni_xAl-LDH (Scheme 3). Step 1, hydroxyl hydrogen of alcohol
- ³⁰ molecule attacks a weak basic Ni-OH^{δ} site on the Ni_xAl-LDH, resulted from an abstraction of proton by the hydroxyl group on the support, to promote the formation of Nialkoxide intermediate at the interface and the simultaneous formation of a water molecule. Step 2, molecular oxygen O₂
- ³⁵ adsorbed on the Au sites near the interface between Au₂₅ clusters and LDH support is directly activated *via* the double linear O_s-Au-O_a model,^{63,64} and the H atom on the β -carbon of the Ni-alkoxide is simultaneously coordinated with Au₂₅ clusters. The adsorption-desorption equilibrium could be
- ⁴⁰ obtained quickly in step 1 or 2 upon the promotion of electron transfer to O_2 .⁶² Step 3, also believed as the ratedetermining step,^{9,61,62} the Ni-alkoxide intermediate undergoes a β -hydride elimination facilitated by the peroxolike species to afford metal-hydride (Au-H^{δ-}) species at the
- ⁴⁵ catalyst interface⁶⁵ accompanied by the formation of the corresponding carbonyl product. The coordinatively unsaturated metal atoms are more active for the cleavage of this C–H bond with the assistance of Au-O-O-Au species. Therefore, the nearly atomic precise Au₂₅ clusters catalyst

⁵⁰ with ultrafine Au particles exhibited much higher activity.



Scheme 3 The possible reaction pathway of the aerobic oxidation of alcohols over Au₂₅/Ni_xAl-LDH (red balls stand for electron-rich Au).

- Final step, the Au-H^{δ} hydride is oxidized rapidly by adsorbed active oxygen to form a water molecule facilitated by the AlO-H^{δ +} acid sites of the support.¹⁸ Thus, the original metallic sites are recovered to realize the catalytic oxidation cycle. Upon this reaction mechanism, the LDH with best ordered layer structure such as Ni₃Al-LDH providing uniform distribution of Ni₃Al-OH ⁶⁰ groups, is the key factor for the β -H elimination of metal alkoxide by the strongest synergetic effect between the nearly atomic precise gold cluster and the LDH support, besides the promotion effect of the weak Brønsted-base sites on the LDH supports. Moreover, in the absence of oxidant, we surmise that the ⁶⁵ Brønsted acid sites (i.e., AlO-H^{δ +}) on the Ni₃Al-LDH support
- might participate in the reaction with the Au hydride to produce molecular H_2 . We will carry out further studies to elucidate this mechanism in our future work.

Conclusions

- ⁷⁰ We have successfully synthesized a series of Ni-based LDH supported nearly atomic precise Au₂₅ clusters catalysts *via* a modified electrostatic adsorption method of Au₂₅Capt₁₈ onto the pre-dispersed Ni-based LDH followed proper calcinations. Especially, the Au₂₅/Ni_xAl-LDH catalysts exhibit excellent ⁷⁵ activity for aerobic oxidation of 1-phenylethanol under no adventitious base with molecular oxygen as a sole oxidant and the activities increase in an order of Au₂₅/Ni₄Al-LDH < Au₂₅/Ni₂Al-LDH < Au₂₅/Ni₂Al-LDH. The kinetic studies show *E*_a values of 17.91, 15.31, and 21.62 kJ/mol for Au₂₅/Ni₂Al-LDH, Au₂₅/Ni₃Al-LDH, Au₂₅/Ni₃Al-Au₂₅/
- ⁸⁰ LDH and Au₂₅/Ni₄Al-LDH in toluene and 19.01, 16.9, and 22.56 kJ/mol under solvent-free conditions, respectively. The catalyst Au₂₅/Ni₃Al-LDH behaves the highest activity owing to the strongest Au₂₅-LDH synergistic effect between the ultrafine Au₂₅ clusters (~0.9 nm) with most negative charge on the clusters'
 ⁸⁵ surface and the LDH support with most Ni-OH sites from the best layer orderliness. We believe that the layer orderliness of the LDH supports affect directly the synergistic effect of Au₂₅ and Ni_xAl-LDH, that is, the higher orderliness of the LDH supports, the stronger interaction between Au₂₅ and supports and the higher

activity of 1-phenylethanol oxidation besides the ultrafine clusters facilitate the aerobic oxidation of alcohols. The similar regularity is also found in Au_{25}/Ni_xMn -LDH and $Au_{25}/Ni_{3-x}Mn_xFe$ -LDH systems though these two systems give lower 1-

⁵ phenylethanol oxidation activity than Au₂₅/Ni₃Al-LDH. These findings may provide new insights into atomic-scale design of environmentally benign and reusable LDH-based Au clusters catalysts for variety of highly efficient heterogeneous catalysis processes.

10 Acknowledgements

This work was supported by National Natural Science Foundation of China, the Fundamental Research Funds for the Central Universities (YS1406) and Beijing Engineering Center for Hierarchical Catalysts.

15 Notes and references

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, P.O. Box 98, Beijing 100029, China. Email: huizhang67@gst21.com; Fax: +8610-6442 5385; Tel.: +8610-6442 5872 (Master students Shuai Wang and Shuangtao Yin contribute 20 equally to this work)

† Electronic Supplementary Information (ESI) available: Details in experimental and further characterization. See DOI: 10.1039/b000000x/

- 1 M. Haruta, N. Yamada, T. Kobayashi and S. Iijima. J. Catal., 1989, **115**, 301-309.
 - 2 A. Corma and P. Serna. Science., 2006, 313, 332-334.
 - 3 C. Milone, R. Ingoglia, L. Schipilliti, C. Crisafulli, G. Neri and S. Galvagno. J. Catal., 2005, 236, 80-90.
- 4 S. Carrettin, J. Guzman and A. Corma. *Angew. Chem. Int. Ed.*, 2005, **44**, 2242-2245.
- 5 M. Conte, A. F. Carley, G. Attard, A. A. Herzing, C. J. Kiely and G. J. Hutchings. J. Catal., 2008, 257, 190-198.
- 6 N. F. Zheng, G. D. Stucky, ChemCommun., 2007, 3862-3864.
- 7 H. Tsunoyama, N. Ichikuni, H. Sakurai and T. Tsukuda. J. Am. Chem. 5 Soc., 2009, **131**, 7086-7093.
- 8 B. Nkosi, M. D. Adams, N. J. Coville and G. J. Hutchings. J. Catal., 1991, 128, 378-386.
- 9 A. Corma and H. Garcia. Chem. Soc. Rev., 2008, 37, 2096-2126.
- 10 H. Tsunoyama, H. Sakurai and T. Tsukuda. Chem. Phys. Lett., 2006, 429, 528-532.
- 11 A. Abad, P. Concepcion, A. Corma and H. Garcia. *Angew. Chem. Int. Ed.*, 2005, **44**, 4066–4069.
- 12 A. Villa, M. Schiavoni and L. Prati. *Catal. Sci. Technol.*, 2012, **2**, 673 682.
- ⁴⁵ 13 P. S. Braterman, Z. P. Xu and F. Yarberry, in Handbook of Layered Materials, ed. S. M. Auerbach, K. A. Carrado and P. K. Dutta, Marcel Dekker, New York, 2004, p. 373.
- 14 H. Zhang, K. Zou, S. H. Guo and X. Duan. J. Solid State Chem., 2006, 179, 1792-1801.
- ⁵⁰ 15 B. M. Choudary, M. L. Kantam, A. Rahman, C. V. Reddy and K. K. Rao. Angew. Chem. Int. Ed., 2001, 40, 763-766.
- 16 H. Zhang, G. Y. Zhang, X. Bi and X. T. Chen. J. Mater. Chem. A., 2013, 1, 5934-5942.
- T. Mitsudome, A. Noujima, T. Mizugaki, K. Jitsukawa and K. Kaneda.
 Adv. Synth. Catal., 2009, **351**, 1890-1896.
- 18 W. H. Fang, J. S. Chen, Q. H. Zhang, W. P. Deng and Y. Wang. *Chem. Eur. J.*, 2011, **17**, 1247-1256.
- 19 P. Liu, Y. J. Guan, R. A. v. Santen, C. Li and E. J. M. Hensen. *Chem. Commun.*, 2011, **47**, 11540-11542.
- 60 20 J. Wang, X. J. Lang, B. Zhaorigetu, M. L. Jia, J. Wang, X. F. Guo and J. C. Zhao. *ChemCatChem.*, 2014, 6, 1737-1747.
 - 21 R. C. Jin. Nanoscale., 2010, 2, 343-362.
 - 22 T. Takei, T. Akita, I. Nakamura, T. Fujitani, M. Okumura, K. Okazaki, J. Huang, T. Ishida and M. Haruta. *Adv. Catal.*, 2012, **55**, 1-126.

- 65 23 Y. M. Liu, H. Tsunoyama, T. Akita and T. Tsukuda. J. Phys. Chem. C., 2009, 113, 13457-13461.
 - 24 S. H. Xie, H. Tsunoyama, W. Kurashige, Y. Negishi and T. Tsukuda. ACS Catal., 2012, 2, 1519-1523.
- 25 Y. Liu, H. Tsunoyama, T. Akita and T. Tsukuda. *Chem. Commun.*, 2010, **46**, 550-552.
- 26 Y. M. Liu, H. Tsunoyama, T. Akita, S. Xie and T. Tsukuda. ACS Catal., 2011, 1, 2-6.
- 27 M. Z. Zhu, E. Lanni, N. Garg, M. E. Bier and R. C. Jin. J. Am. Chem. Soc., 2008, 130, 1138-1139.
- 75 28 C. L. Yu, G. Li, S. Kumar, H. Kawasaki and R. C. Jin. J. Phys. Chem. Lett., 2013, 4, 2847-2852.
 - 29 Z. L. Wu, D.-e. Jiang, A. K. P. Mann, D. R. Mullins, Z.-A. Qiao, L. F. Allard, C. Zeng, R. C. Jin and S. H. Overbury. J. Am. Chem. Soc., 2014, 136, 6111-6122.
- 80 30 G. Li, D.-e. Jiang, C. Liu, C. L. Yu and R. C. Jin. J. Catal., 2013, 306, 177-183.
- 31 L. Li, L. G. Dou and H. Zhang. Nanoscale., 2014, 6, 3753-3763.
- 32 S. Kumar and R. Jin. Nanoscale., 2012, 4, 4222-4227.
- 33 M. Z. Zhu, W. T. Eckenhoff, T. Pintauer and R. C. Jin. J. Phys. Chem. C., 2008, **112**, 14221-14224.
- 34 Y. Negishi, T. Tsukuda. J. Am. Chem. Soc., 2003, 125, 4046-4047.
 35 J. Simard, C. Briggs, A. K. Boal and V. M. Rotello. Chem. Commun., 2000, 1943-1944.
- 36 V. Rives and S. Kannan. J. Mater. Chem., 2000, 10, 489-495.
- 90 37 J. T. Kloprogge and R. L. Frost. J. Solid State Chem., 1999, 146, 506-515.
- 38 V. Prevot, N. Caperaa, C. Taviot-Guého and C. Forano. Cryst. Growth Des., 2009, 9, 3646-3654.
- 39 F. Rouquerol, J. Rouquerol and K. Sing. Adsorption by Powders and Porous Solids: Principles, Methodology and Applications. Academic Press, London, 1999.
- 40 F. Mi, X. T. Chen, Y. W. Ma, S. T. Yin, F. L. Yuan and H. Zhang. *Chem. Commun.*, 2011, 47, 12804-12806.
- 41 L. Wang, J. Zhang, X. J. Meng, D. F. Zheng and F. S. Xiao. *Catal. Today.*, 2011, **175**, 404-410.
- 42 T. Mitsudome, A. Noujima, T. Mizugaki, K. Jitsukawa and K. Kaneda. Adv. Synth. Catal., 2009, 351, 1890-1896.
- 43 D.-en. Jiang, S. H. Overbury and S. Dai. J. Phys. Chem. Lett., 2011, 2, 1211-1215.
- ¹⁰⁵ 44 J. A. Smith, M. Josowicz, M. Engelhard, D. R. Baer and J. Janata. *Phys. Chem. Chem. Phys.*, 2005, **7**, 3619-3625.
 - 45 F. Wang, W. Ueda and J. Xu. Angew. Chem. Int. Ed., 2012, 51, 3883-3887.
- 46 M. Wei, X. Y. Xu, X. R. Wang, F. Li, H. Zhang, Y. L. Lu, M. Pu, D. G. Evans and X. Duan. *Eur. J. Inorg. Chem.*, 2006, 2831-2838.
- 47 P. J. Sideris, U. G. Nielsen, Z. Gan and C. P. Grey. *Science.*, 2008, **321**, 113-117.
- 48 M. J. Climent, A. Corma, P. D. Frutos, S. Iborra, M. Noy, A. Veity and P. Concepción. J. Catal., 2010, 269, 140-149.
- ¹¹⁵ 49 B. Yoon, H. Häkkinen, U. Landman, A. S. Wörz, J. M. Antonietti, S. Abbet, K. Judai and U. Heiz. *Science.*, 2005, **307**, 403-407.
 - 50 A. Fielicke, G. Helden, G. Meijer, B. Simard, and D. M. Rayner. J. *Phys. Chem. B.*, 2005, **109**, 23935-23940.
 - 51 M. S. Chen and D. W. Goodman. Acc. Chem. Res., 2006, **39**, 739-746.
- 52 H. J. Freund. *Catal. Today.*, 2006, **117**, 6-14.
 53 N. Bogdanchikova, A. Pestryakov, I. Tuzovskaya, T. A. Zepeda, M. H. Farias, H. Tiznado and O. Martynyuk. *Fuel.*, 2013, **110**, 40-47.
 - 54 J. Kim, E. Samano and B. E. Koel. J. Phys. Chem. B., 2006, 110, 17512-17517.
- 125 55 M. S. Chen, Y. Cai, Z. Yan and D. W. Goodman. J. Am. Chem. Soc., 2006, 128, 6341-6346.
- 56 F. Boccuzzi, A. Chiorino, S. Tsubota and M. Haruta. J. Phys. Chem., 1996, 100, 3625–3631.
- 57 A. Villa, C. E. Chan-Thaw, G. M. Veith, K. L. More, D. Ferri and L. ¹³⁰ Prati. *ChemCatChem.*, 2011, **3**, 1612-1618.
 - 58 A. L. McKenzie, C. T. Fishel, R. J. Davis. J. Catal., 1992, 138, 547-561.
 - 59 H. Tsunoyama, H. Sakurai, Y. Negishi and T. Tsukuda. J. Am. Chem. Soc., 2005, **127**, 9374-9375.

- 60 Y. D. Kim, M. Fischer and G. Gantefor, *Chem. Phys. Lett.*, 2003, **377**, 170–176.
- 61 A. Abad, P. Concepción, A. Corma and H. García. Angew. Chem. Int. Ed., 2005, 44, 4066-4069.
- ⁵ 62 S. Nishimura, Y. Yakita, M. Katayama, K. Higashimine and K. Ebitani. *Catal. Sci. Technol.*, 2013, **3**, 351-359.
- 63 K. J. Sun, M. Kohyama, S. Tanaka and S. Takeda. *ChemCatChem.*, 2013, **5**, 2217-2222.
- 64 K. J. Sun, M. Kohyama, S. Tanaka, and S. Takeda. J. Phys. Chem. A., 20 2012, **116**, 9568-9573.
- 65 M. Conte, H. Miyamura, S. Kobayashi and V. Chechik. J. Am. Chem. Soc., 2009, 131, 7189-7196.

Catalysis Science & Technology Accepted Manuscript

Table of Contents (TOC)



5 Nearly atomic precise Au₂₅/Ni_xAl-LDH catalysts obtained via modified electrostatic adsorption of Au₂₅Capt₁₈ onto predispersed Ni_xAl-LDH followed proper calcination shows extraordinary alcohol oxidation property with O2 due to ultrafine Au cluster, ordered LDH layer and strong Au25-LDH synergy.