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# Supporting Information

## A facile route to encapsulate ultrasmall Ni clusters within the pore channels of AlPO-5

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### Experimental

#### Raw Materials

All materials were obtained from commercial suppliers and used without further purification. Nickel chloride hexahydrate, Phosphoric acid (85wt% in H<sub>2</sub>O), glycerol, 1,2-Propanediol, Nickel nitrate hexahydrate, Ethylene glycol, and diethylenetriamine were purchased from Aladdin Industrial Corporation, pseudo-boehmite (Al<sub>2</sub>O<sub>3</sub>≥70%) were purchased from Zibo Baida Chemical China Co., Ltd. Ammonium fluoride from sinopharm chemical reagent Co., Ltd .

#### Catalysts preparation

For Ni@AlPO-5 catalyst, firstly Ni(deta)<sub>2</sub>-AlPO-5 was prepared by using nickel-amine complexes, [Ni(diethylenetriamine)<sub>2</sub>]<sup>2+</sup>, as templating agent. Typically, 0.41 mL of phosphoric acid, 0.4855g pseudo-boehmite and 24g water were adequately mixed, to this mixture 0.55g Ni(deta)<sub>2</sub>Cl<sub>2</sub> and 0.064g NH<sub>4</sub>F were finally added. After stirring for 3 hours, the resulting homogeneous gel was transferred into a Teflon-lined autoclave and heated at 190 °C for 26 h, then cooled, washed with deionized water and dried at room temperature. Secondly, the dried Ni(deta)<sub>2</sub>-AlPO-5 samples were heated at 350 °C for 4 hours, and then 600 °C for 6 hours, both under N<sub>2</sub> atmosphere.

For Ni/AlPO-5 catalyst, firstly, TEA-AlPO-5 was prepared with triethylamine

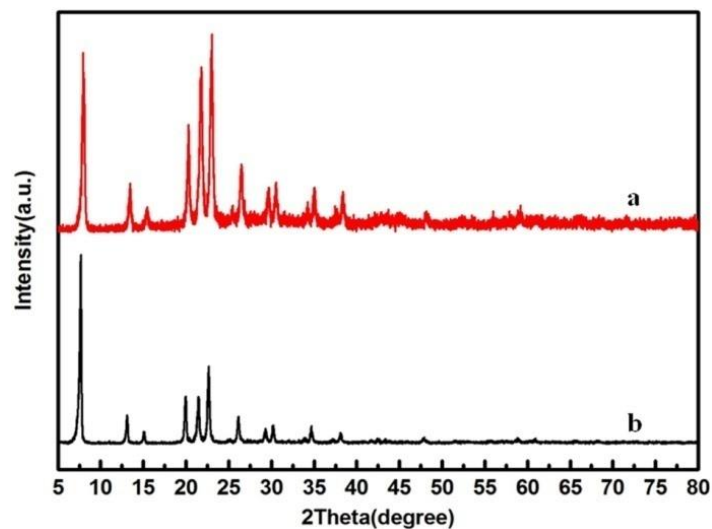
(TEA) as templating agent, the synthetic process is similar to that mentioned above. Before loading Ni(II) ions in AlPO-5, the organic species occluded in TEA-AlPO-5 was calcined to produce a porous material (AlPO-5) at 350 °C for 4 hours, and then 600 °C for 6 hours under air. Secondly, certain amount of Ni (II) was loaded in AlPO-5 by using impregnation method and then Ni (II) was reduced to obtain Ni/AlPO-5 under H<sub>2</sub> atmosphere at 500 °C for 3h. Powder XRD pattern was used to confirm the phase, powder XRD patterns of Ni/AlPO-5 (a) and AlPO-5(b) after calcination in air were shown in Figure S1.

### **Catalysts characterization**

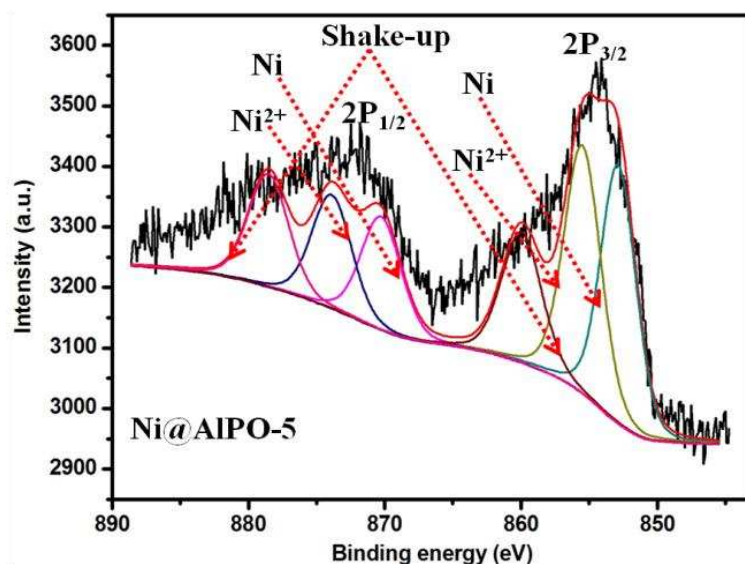
The powder X-ray patterns were collected on Rigaku Miniflex II X-ray diffractometer using a Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). High resolution TEM images were obtained using a JEOL JEM-2100 microscope, operated at 200kV with a LaB<sub>6</sub> filament. X-ray photoelectron spectroscopy (XPS) spectra were acquired on thermo ESCALAB 250XI apparatus with an Al Ka source ( $h\nu=1486.6 \text{ eV}$ ). The BET surface area of the catalysts was determined using a Micromeritics ASAP 2020. Fourier transformation infrared (FT-IR) spectroscopy were recorded on a Shimadzu IR Affinity-1 spectrometer. Thermogravimetry-mass spectrometry (TG-MS) was conducted on Pfeiffer Omni Star under N<sub>2</sub> atmosphere with a heating rate of 5 °C /min.

### **Catalytic Test**

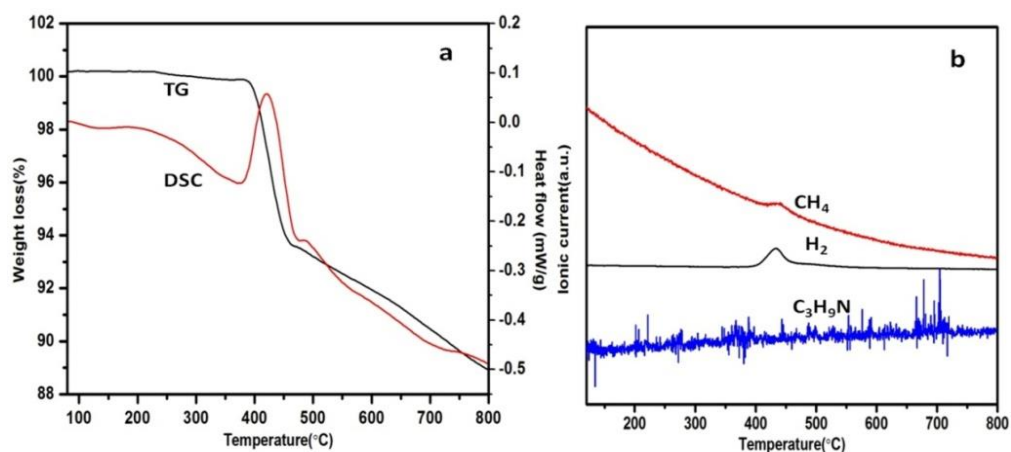
Typically, glycerol solution (25 wt% in water) and catalysts (glycerol/Ni=20 molar ratio) were loaded in the Teflon-lined autoclave, the reactor was pressurized with 6 MPa H<sub>2</sub> after the air had been flushed out and heated at 200 °C for several hours under vigorously stirring (600 rpm). After reaction, catalysts were filtered off from the reaction system and the reaction liquid was quantified by high-performance liquid chromatography (HPLC) equipped with refractive index detector (RID) detector. Aminex HPX-87 H column (Bio-Rad) was operated at 60 °C with 0.01mol/L H<sub>2</sub>SO<sub>4</sub> solution as eluent flowing at 0.5 mL/min.



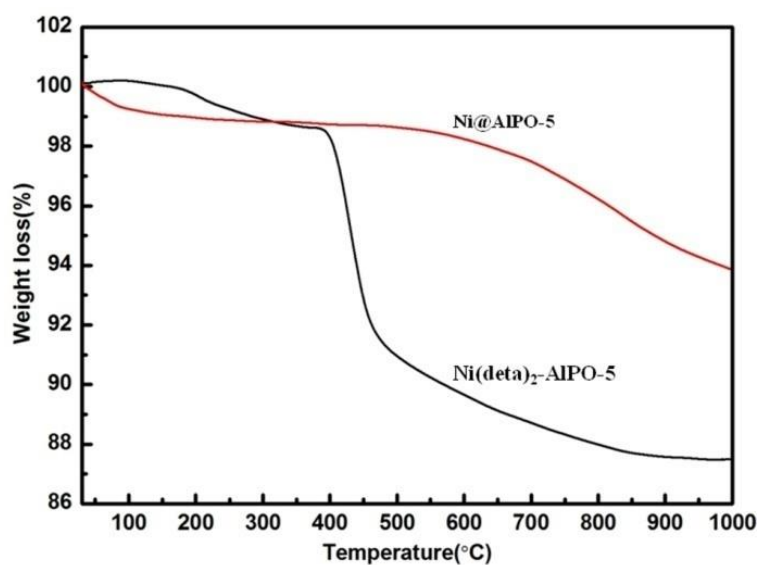
**Figure S1** Powder XRD patterns of Ni/AlPO-5 (a) and AlPO-5(b) after calcination in air



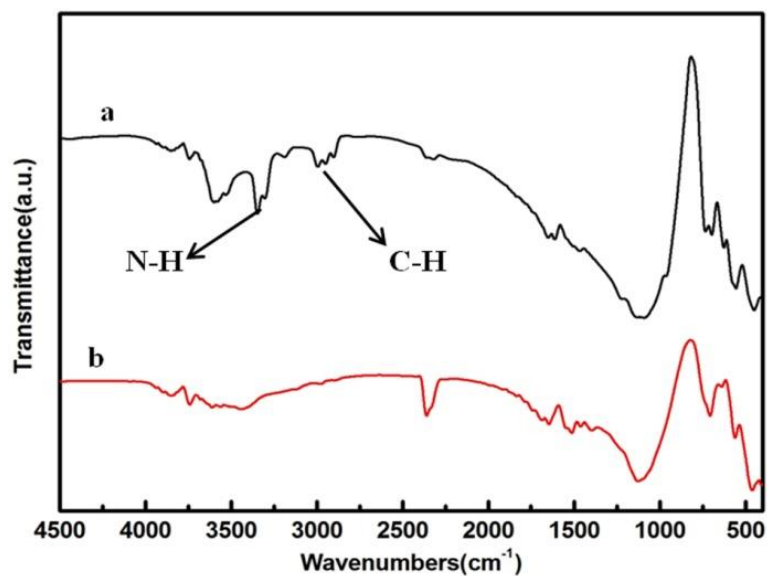
**Figure S2** XPS spectra of Ni 2P in Ni@AlPO-5. The Ni 2P spectrum exhibits two contributions,  $2P_{3/2}$  and  $2P_{1/2}$ , located around 852.8 and 870.2 eV respectively in catalyst Ni@AlPO-5, which means most of Ni(II) ions in Ni(deta)<sub>2</sub>-AlPO(F)-5 could be reduced to zero-valent Ni by heat treatment under N<sub>2</sub>.



**Figure S3** (a) TG-DSC curves and (b) MS spectrum for Ni(deta)<sub>2</sub>-AIPO-5 heated under N<sub>2</sub> atmosphere. The endothermic peak around 420 °C on DSC curve is attributed to the thermal decomposition of nickel amine complexes, accompanying with the formation of CH<sub>4</sub>, H<sub>2</sub>, C<sub>3</sub>H<sub>9</sub>N observed on MS spectrum.



**Figure S4** TG curves of the as-synthesized Ni(deta)<sub>2</sub>-AIPO-5 and Ni@AIPO-5



**Figure S5** FT-IR spectra of the samples Ni(deta)<sub>2</sub>-AIPO-5(a) and Ni@AIPO-5(b)

**Table S1** The catalytic performance of the as-prepared catalyst.<sup>a</sup>

Entry	Catalysts	Time (h)	Conversion (%)	Selectivity(%) <sup>b</sup>	
				1,2-PDO	EG
1	Ni@AIPO-5	12	5.06	92.68	nd <sup>c</sup>
2	Ni/AIPO-5	12	30.15	68.65	1.52
3	none	12	-	-	-

<sup>a</sup>Reaction Conditions: 25 g glycerol aqueous solution (25 wt%), glycerol/Ni=20 (molar ratio), 200 °C, 6 MPa H<sub>2</sub>, 12h; 1,2-Propanediol (1,2-PDO), Ethylene glycol (EG); <sup>b</sup>Others include: propanol, ethanol; <sup>c</sup>nd: Not detected;