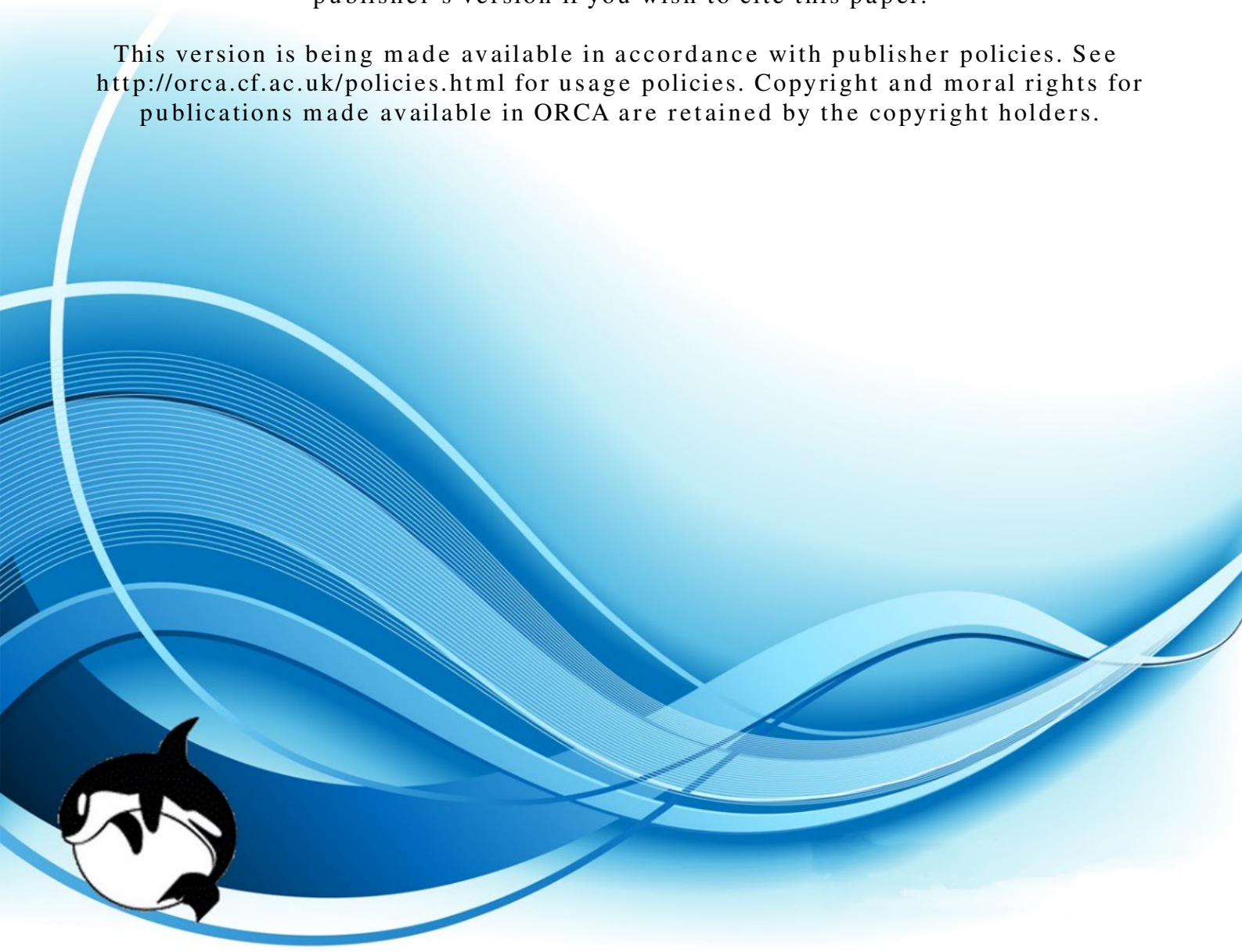

Supporting Information

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_2O), glycerol, 1,2-Propanediol, Nickel nitrate hexahydrate, Ethylene glycol, and diethylenetriamine were purchased from Aladdin Industrial Corporation, pseudo-boehmite (Al_2O_3≥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)$_2$-AlPO-5 was prepared by using nickel-amine complexes, [Ni(diethylenetriamine)$_2$]$^{2+}$, 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)$_2$Cl$_2$ and 0.064g NH_4F were finally added. After stirring for 3 hours, the resulting homogeneous gel was transferred into a Teflon-lined autoclave and heated at 190 ^oC for 26 h, then cooled, washed with deionized water and dried at room temperature. Secondly, the dried Ni(deta)$_2$-AlPO-5 samples were heated at 350 ^oC for 4 hours, and then 600 ^oC for 6 hours, both under N_2 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_2 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-Kα radiation (λ = 1.5418 Å). High resolution TEM images were obtained using a JEOL JEM-2100 microscope, operated at 200kV with a LaB_6 filament. X-ray photoelectron spectroscopy (XPS) spectra were acquired on thermo ESCALAB 250XI apparatus with an Al Ka source (hv=1486.6 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 Shimadu IR Affinity-1 spectrometer. Thermogravimetry-mass spectrometry (TG-MS) was conducted on Pfeiffer Omni Star under N_2 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_2 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_2SO_4 solution as eluent flowing at 0.5 mL/min.

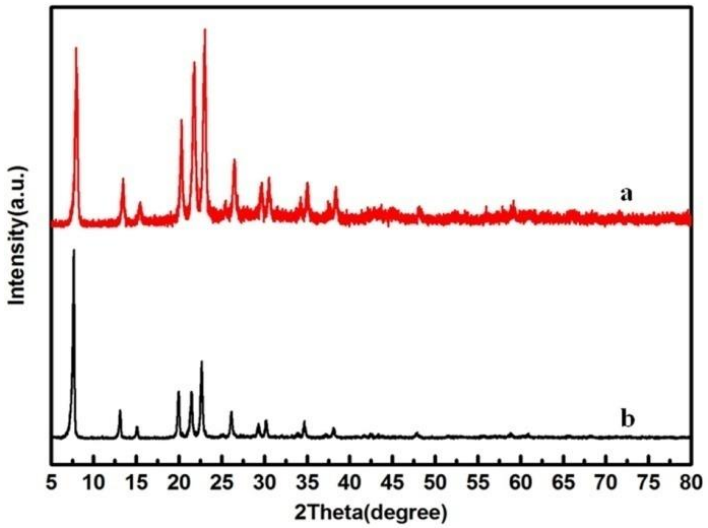

Figure S1 Powder XRD patterns of Ni/AlPO-5 (a) and AlPO-5(b) after calcination in air

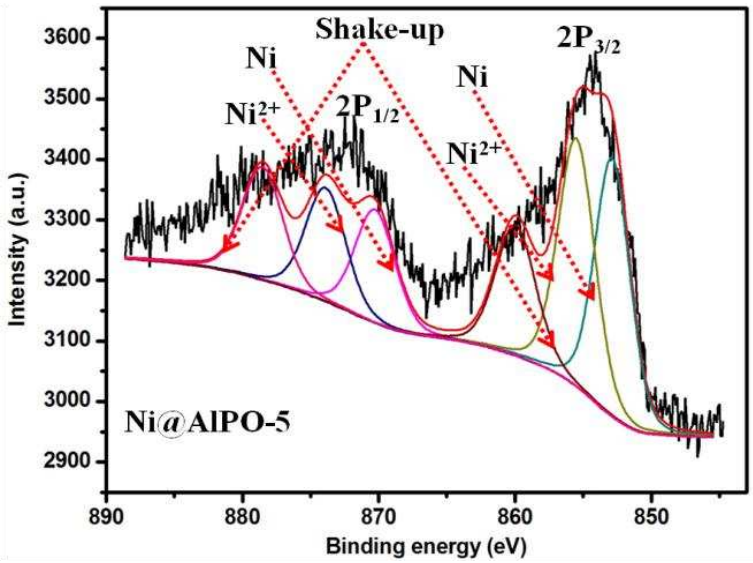

Figure S2 XPS spectra of Ni 2P in Ni@AlPO-5.The Ni 2P spectrum exhibits two contributions, $2P_{3/2}$ and $2P_{1/2}$, located around 852.8 and 870.2eV respectively in catalyst Ni@AlPO-5, which means most of Ni(II) ions in $Ni(deta)_2$-AlPO(F)-5 could be reduced to zero-valent Ni by heat treatment under N_2.

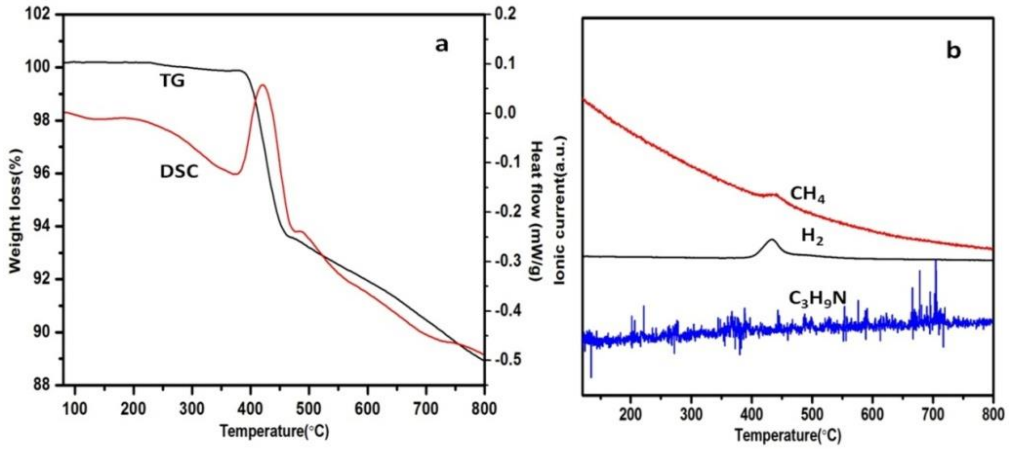

Figure S3 (a) TG-DSC curves and (b) MS spectrum for Ni(deta)$_2$-AlPO-5 heated under N_2 atmosphere. The endothermic peak around 420 ºC on DSC curve is attributed to the thermal decomposition of nickel amine complexes, accompanying with the formation of CH_4, H_2, C_3H_9N observed on MS spectrum.

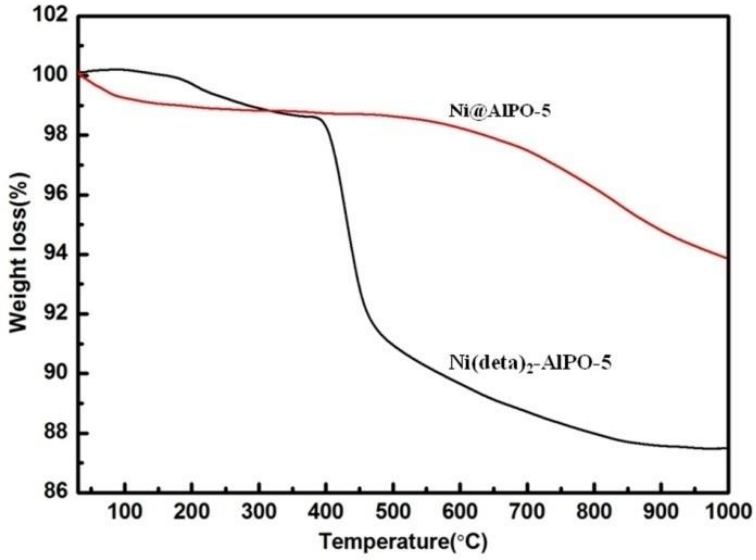

Figure S4 TG curves of the as-synthesized Ni(deta)$_2$-AlPO-5 and Ni@AlPO-5

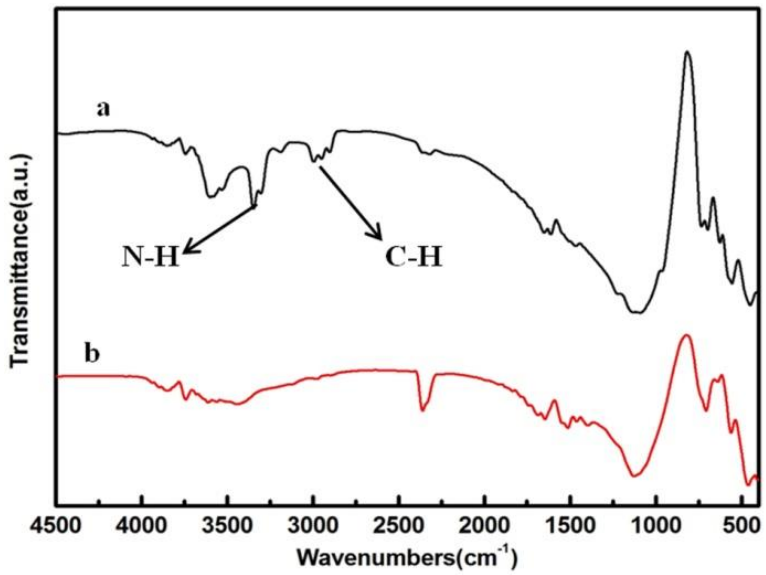

Figure S5 FT-IR spectra of the samples Ni(deta)$_2$-AlPO-5(a) and Ni@AlPO-5(b)

Table S1 The catalytic performance of the as-prepared catalyst.[a]

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

[a]Reaction Conditions: 25 g glycerol aqueous solution (25 wt%), glycerol/Ni=20 (molar ratio),200 °C, 6 MPa H_2,12h; 1,2-Propanediol (1,2-PDO), Ethylene glycol (EG); [b] Others include: propanol, ethanol; [c]nd: Not detected;