Supporting Information

Amino-Modified Halloysite Nanotube-Supported Nickel Catalysts for Efficient Reductive Amination of Biomass Aldehydes and Ketones

Weihong Li [a], *Nan Zhong* [b], *Yifei Yin* [b], *Weiming Xiao* [a], *Shunmin Ding* [a], *Rongping Zhou* [c], *Chao Chen* [a], *Shengjun Deng* [a] *

[a] Key Laboratory of Jiangxi Province for Environment and Energy Catalysis, college of Chemistry, Nanchang University, Nanchang, Jiangxi 330031, P.R. China
[b] School of Pharmacy, Nanchang University, Nanchang, Jiangxi 330031, P.R. China
[c] The first affiliated hospital of Nanchang university, Jiangxi 330006, P.R. China

* Corresponding author：Shengjun Deng. E-mail: shjdeng@ncu.edu.cn

S1. Materials and Characterization Instruments

Halloysite Nanotubes ($Al_2Si_2O_5(OH)_4·2H_2O$, 98%) was purchased from Yuanxin Nano technology Co., Ltd. Sodium borohydride ($NaBH_4$, 97%) was purchased from Shanghai Qingxi Chemical Technology Co., Ltd. Isopropanol ($(CH_3)_2CHOH$, 99%) was purchased from Xilong Scientific Co., Ltd. Nickel nitrate hexahydrate ($Ni(NO_3)_2·6H_2O$, 98%) were purchased from Shanghai Aladdin Biochemical Science and Technology Co., Ltd. γ-aminopropyl triethoxysilane (APTES, 98%), anhydrous sodium bicarbonate ($NaHCO_3$, 98%), dodecane (99%), and furfural (FAL, 99%) were purchased from Innochem Reagent Co., Ltd. All chemical reagents in chemical analysis purity commercially obtained were used directly without further purification.

The Ni content of catalyst was determined by using Agilent Technologies 5100 Inductively Coupled Plasma Optical Emis-sion Spectrometer (ICP-OES).

X-ray powder diffraction (XRD) patterns were recorded on a Persee XD-3X benchtop X-ray diffractometer with Cu Kα (k = 0.15406 nm) radiation at 40 kV and 40 mA with scanning rate of 4 °/min in the range of 10 ° - 70 ° (2ϑ).

FT-IR spectra (FT-IR) was collected with an Agilent Cary 630 Fourier Transform Infrared Spectrometer. Potassium bromide was used for sample preparation and analysis, with a scanning wavenumber range of 4000-400 cm^{-1}. Transform infrared spectra of pyridine adsorption (Py-IR) was similar to the above process, except that pyridine was added dropwise to the prepared sample and then dried using an infrared lamp, repeating the above steps multiple times.

The specific surface area and pore structure of the sample were measured according to Brunauer-Emmett-Teller (BET) procedure on a Micromeritics ASAP 2020 analyzer. The sample was degassed under vacuum at 150 ℃ for 12 h prior to the physisorption measurements. The pore volume and pore size distribution were determined by BJH method.

X-ray photoelectron spectroscopy measurements (XPS) of the samples were analyzed on a Thermo Scientific K-Alpha equipped with a monochromatic Al Kα source (hν = 1486.6 eV). The C 1s peak of adventitious carbon at 284.8 eV was referred to rectify the binding energy in XPS spectra.

TEM images were acquired using a JEOL JEM-2100 microscope configured with an energy-dispersive X-ray spectroscopic analyzer conducted at an acceleration voltage of 200 kV. The sample was dispersed by sonication in hydrous ethanol. Then, the suspended solution was dropped and dried on carbon film-coated 400 mesh copper grids for morphological observation.

Temperature programmed desorption of H_2, CO_2 and NH_3 (H_2-TPD, CO_2-TPD and NH_3-TPD) experiments were carried out on a Micromeritic- Auto-Chem II 2920 chemisorption analyzer combined with a thermal conductivity detector and a computer-controlled furnace. Prior to measurement, 50 mg of sample was placed in a U-shaped quartz tube, and kept at 150 ℃ for 1 h in pure argon (30 mL/min), then cooled to room temperature under argon. The system was purged with H_2 for 1 h at 30 mL/min to remove the physically absorbed argon; Subsequently, the pure argon was switched into the system again for 30 min to purge H_2. Finally, the sample was heated to 400 ℃ at a heating rate of 10 ℃/min and desorption signals were monitored by TCD. The measurement methods for NH_3-TPD and CO_2-TPD are similar to those for H_2-TPD.

S2. Preparation of Ni/Al_2O_3 and Ni/SiO_2

Typically, the Al_2O_3 and $Ni(NO_3)_2 \cdot 6H_2O$ with adjustable Al_2O_3: Ni mass ratio were added to 40 mL of deionized water. The reaction mixture was stirred for 1.5 h, then stirred for another 0.5 h in an ice water bath. Afterwards, a fresh prepared ice aqueous solution of sodium borohydride ($NaBH_4$ is 5 equiv to Ni) was added into the above mixture, and then stirred for 1 h. The precipitation was obtained by filtration, washed three times with deionized water, and washed once with ethanol. After vacuum drying, Ni/Al_2O_3 was obtained. The Ni/SiO_2 was prepared using the procedure similar to that of Ni/Al_2O_3 except that SiO_2 was used in the place of Al_2O_3.

S3. Cycle experiment

Typically, 1 mmol of FAL, 0.05 g of 10%Ni-WHNT, and 15 mL of isopropanol were added and mixed in a 100 mL a stainless-steel high-pressure reactor. After sealed, the reactor was rinsed 7-10 times with H_2 (99.999%). After 0.5 MPa H_2 and 0.3 MPa NH_3 were filled, the experiments were conducted at the desired temperature (90 ℃) and a specified reaction time (3 h) under constant magnetic stirring (450 rpm). After the reaction, the autoclave was naturally cooled down to room temperature and depressured slowly. The catalyst was separated by centrifugation, washed three times with ethanol, and dried at 70 ℃ in a vacuum oven. The recovered catalyst was used again another five times for the same reaction using the same procedure. The reaction mixture was analyzed by an Agilent 5977A MSD gas chromatography-mass spectrometry (GC-MS) employing HP-5 (30 m × 0.25 mm × 0.25 μm) column and thermal conductivity detector (TCD). The conversion and selectivity for the reaction were calculated as following:

$$\text{Conversion (\%)} = \left(1-\frac{moles\ of\ residual\ furfural}{moles\ of\ initial\ furfural}\right) \times 100\%$$

$$\text{Selectivity (\%)} = \frac{moles\ of\ target\ product}{moles\ of\ total\ products} \times 100\%$$

S4. Shielding experiment

Triethylamine and benzoic acid served as shielding agents for acidic and basic sites, respectively. Initially, a certain amount (1: 1 molar ratio to FAL) of the shielding agent was mixed with the dispersion solution of the catalyst, allowing the shielding agent to interact with the catalyst for 30 min. The dispersion solution consists of 1 mmol FAL, 50 μL dodecane, and 15 mL isopropanol. Subsequently, FAL was added to the solution for reaction.

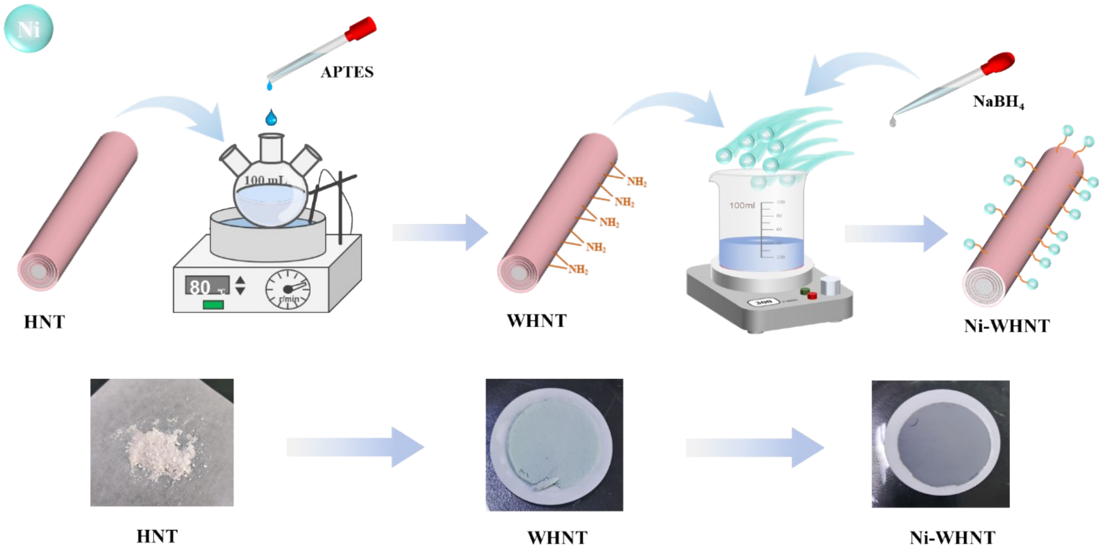


Fig. S1. Schematic illustration of synthesis process of catalyst.

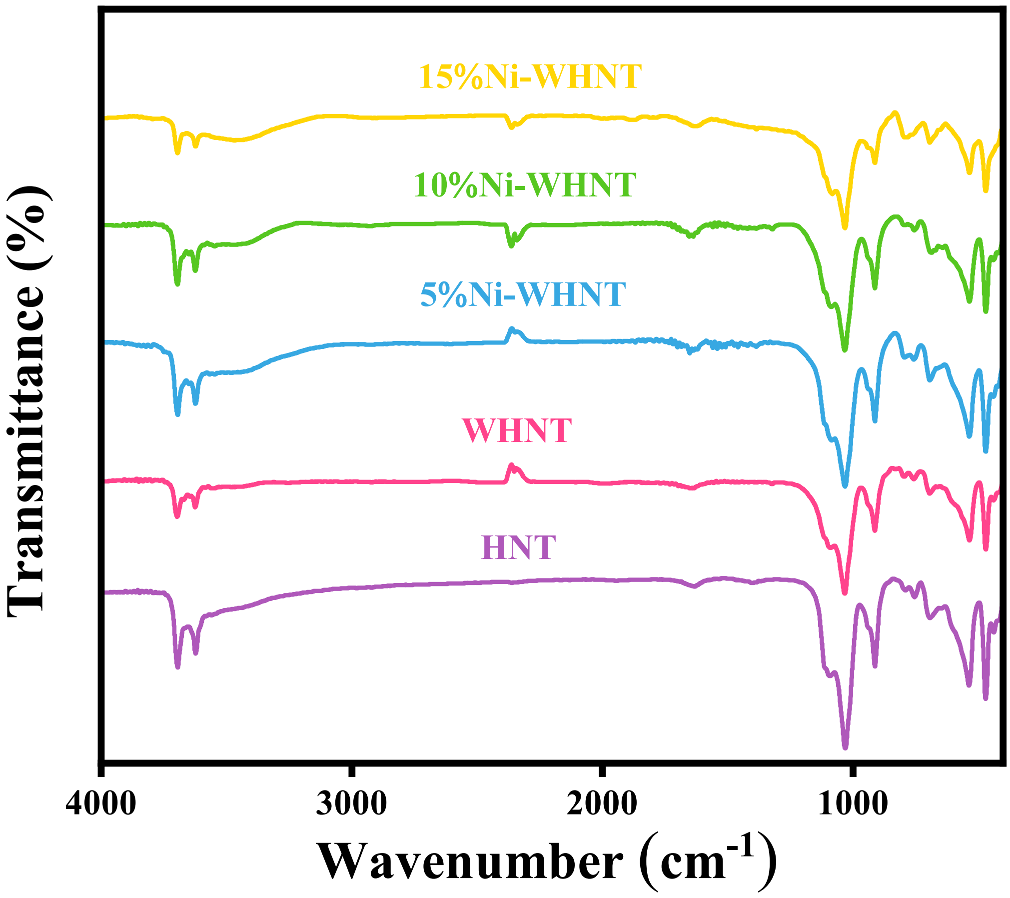


Fig. S2. FT-IR spectra of the typical catalyst samples.

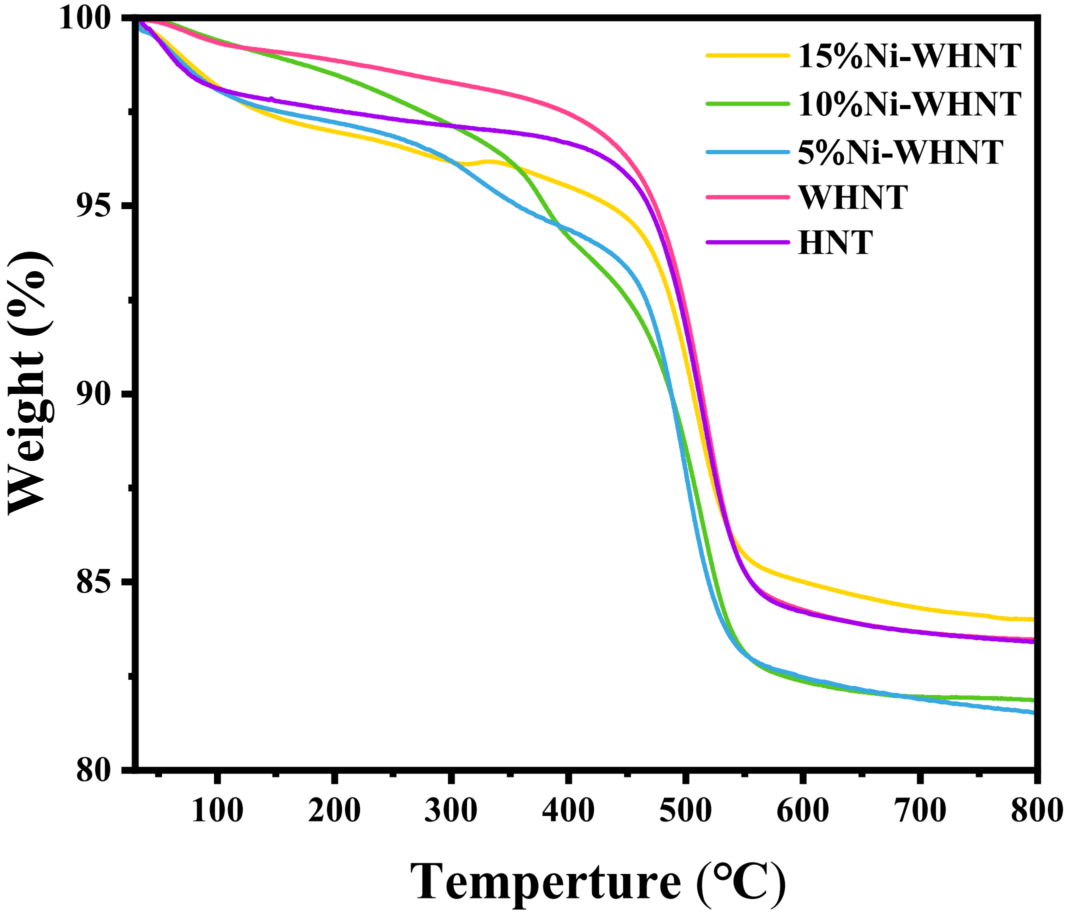


Fig. S3. TGA patterns of the typical catalyst samples.

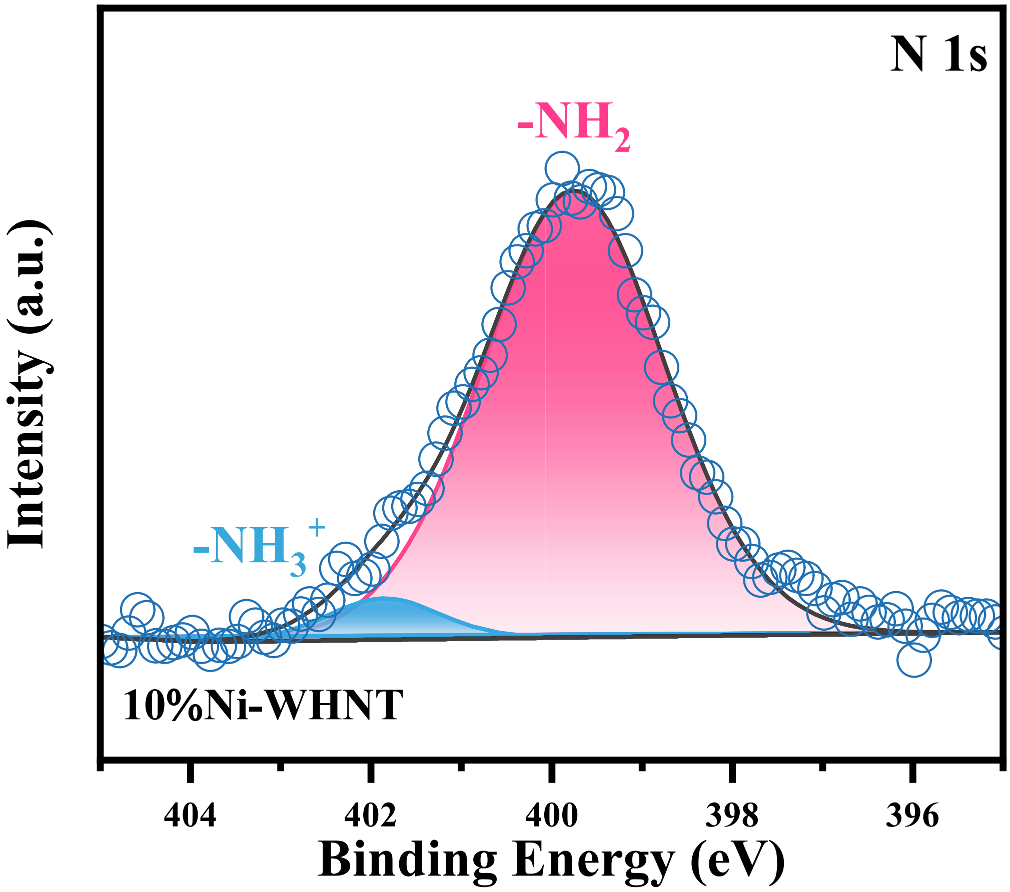


Fig. S4. N 1s XPS spectra of the 10%Ni-WHNT.

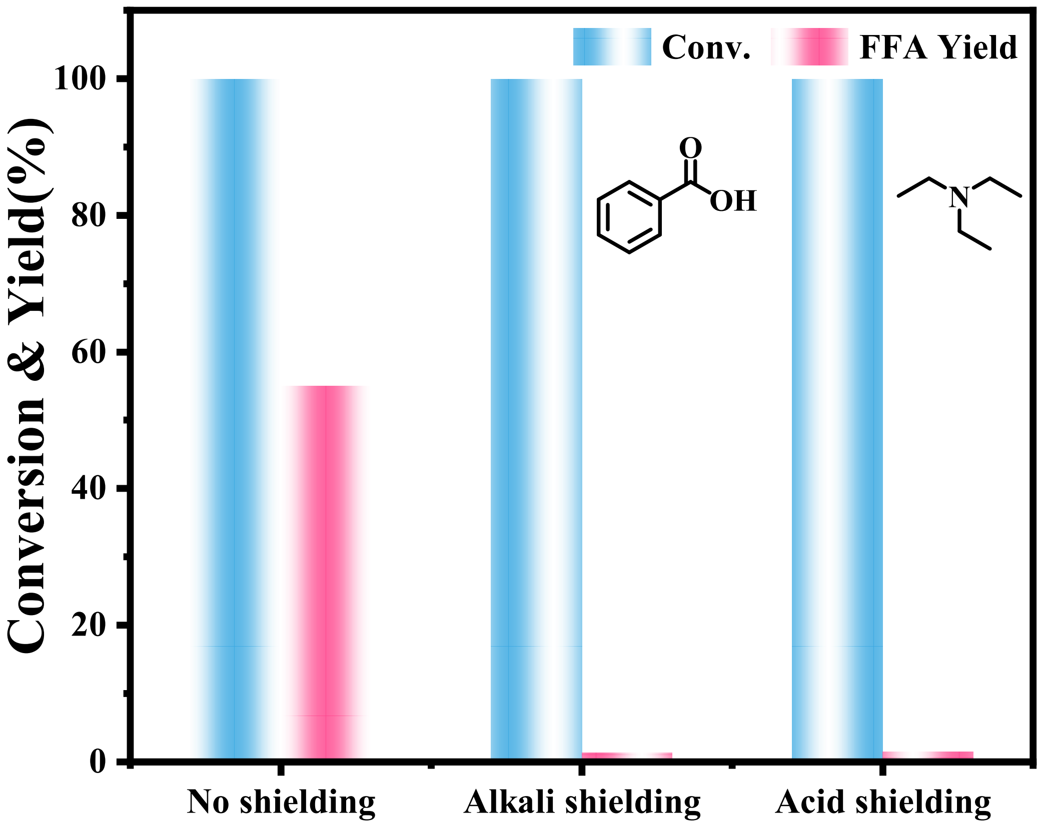


Fig. S5. Catalytic performance of the 10%Ni - WHNT catalyst in presence of different shielding agents at 1 h.

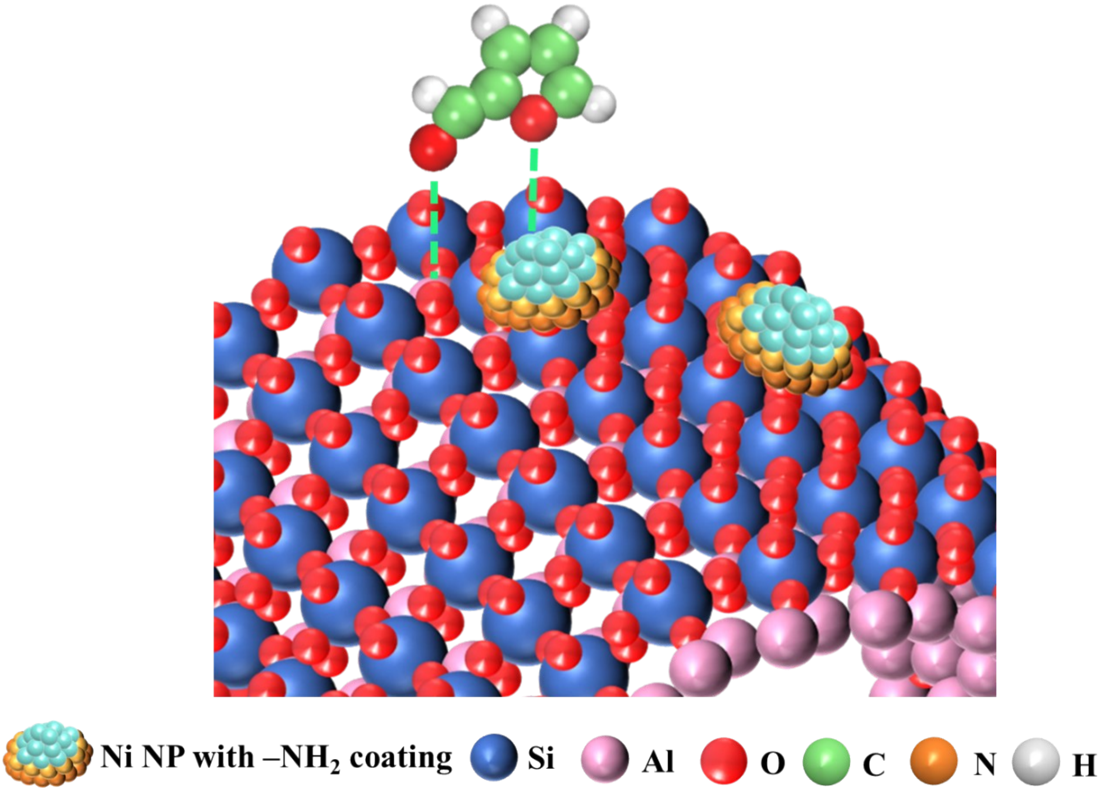


Fig. S6. The adsorption model of furfural on the Ni-WHNT catalyst.

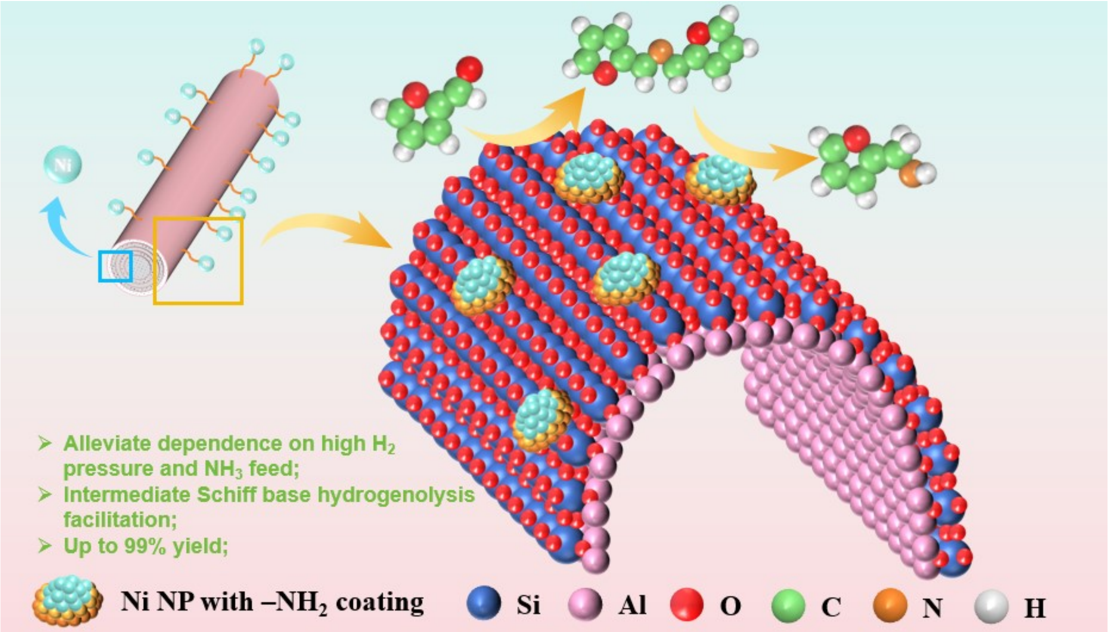


Fig. S7. Possible catalytic mechanism of key steps in tandem reductive amination over the Ni-WHNT catalyst.

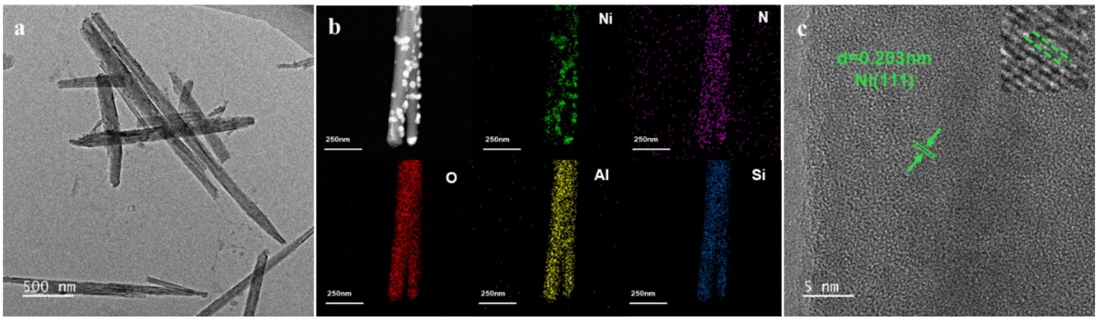
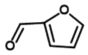
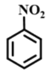
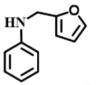
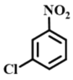
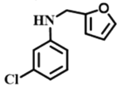
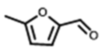
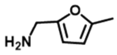
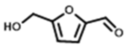
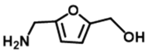
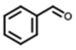
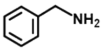
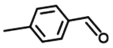
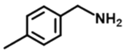


Fig. S8. (a) TEM image, (b) The corresponding EDS mappings, and (c) HRTEM images with enlarged images of the 2%Ni-WHNT catalyst.

Table S1. The Ni content of all samples.

Entry	**Catalysts**	**Ni(wt%)**
1	5%Ni-WHNT	4.63
2	10%Ni-WHNT	9.33
3	15%Ni-WHNT	13.89
4	10%Ni-SiO_2	9.31
5	10%Ni-Al_2O_3	9.28
6	After cycling10%Ni-WHNT	9.25

Table S2. Production of primary amines from various aldehydes and ketones over 10%Ni-WHNT.

Entry	Substrate 1	Substrate 2	Product	Conv. (%)	Yield (%)
1				88	50
2				> 99	> 99
3		NH_3		> 99	> 99
4				> 99	> 99
5				> 99	> 99
6				> 99	96

Reaction conditions: FAL (1 mmol), catalyst (50 mg), isopropanol (15 mL), H_2 (1 MPa), NH_3 (0.4 MPa), 120 °C, 8 h.

Table S3. Particle size of samples calculated based on XRD diffraction peak.

Sample	k	λ	2ϑ	ϑ	Cos ϑ	FWHM	β	D(nm)
HNT	0.890	0.154	11.921	5.961	0.995	0.713	0.012	11.073
	0.890	0.154	20.185	10.092	0.985	1.216	0.021	6.560
	0.890	0.154	23.575	11.787	0.979	4.608	0.080	1.742
	0.890	0.154	35.366	17.683	0.953	1.469	0.026	5.613
	0.890	0.154	38.226	19.113	0.945	1.952	0.034	4.260
	0.890	0.154	55.395	27.697	0.885	3.201	0.056	2.772
	0.890	0.154	62.260	31.130	0.856	0.956	0.017	9.602
WHNT	0.890	0.154	11.541	5.771	0.995	0.685	0.012	11.524
	0.890	0.154	19.896	9.948	0.985	1.331	0.023	5.994
	0.890	0.154	23.540	11.770	0.979	4.158	0.073	1.930
	0.890	0.154	35.025	17.513	0.954	1.481	0.026	5.564
	0.890	0.154	37.943	18.972	0.946	2.086	0.036	3.983
	0.890	0.154	54.874	27.437	0.888	2.230	0.039	3.969
	0.890	0.154	61.941	30.970	0.857	0.672	0.012	13.628

Table S4. TONs of various catalysts and 10%Ni-WHNT for the reductive amination of FAL to FAM.

Catalyst	Load capacity (wt%)	FAM Yield (%)	TON	Ref.
Ni/SiO_2-I-DP	15	90.7	17.7	1
Ni/ Al_2O_3(110)	—	1	0.2	2
Ni/Al_2O_3(111)	—	97	33.4	2
Ni/MC	3.8	88	6.8	3
Ni/ Al_2O_3	10	> 99	11.6	4
Ni_6AlO_X	—	90	2.3	4
Raney Ni	—	> 99	1.3	4
Raney Co	—	98	11.6	5
10%Ni-WHNT	9.3	> 99	12.6	This work

Reference

1. Yang, Y.; Zhou, L.; Wang, X.; et al. Catalytic reductive amination of furfural to furfurylamine on robust ultra-small Ni nanoparticles. *Nano Res*. **2023**, *16*(3), 3719-3729.

2. Wan, Y. J.; Ma, P. F.; Lu, H. L.; et al. External [1 1 1] facets on nanorod gamma alumina boosts catalytic reductive amination of carbonyl compound to primary amine. *J. Catal.* **2024**, *429,* 115–125.
3. Zhang, Y. M.; Yang, H. M.; Chi, Q.; et al. Nitrogen-Doped Carbon-Supported Nickel Nanoparticles: A Robust Catalyst to Bridge the Hydrogenation of Nitriles and the Reductive Amination of Carbonyl Compounds for the Synthesis of Primary Amines. *ChemSusChem*. **2019**, *12*(6), 1246 –1255.
4. Dong, C. L.; Wang, Y. S.; Peng, H. T.; et al. Facile and Efficient Synthesis of Primary Amines via Reductive Amination over a Ni/Al_2O_3 Catalyst. *ACS Sustainable Chem. Eng.* **2021**, *9*(21), 7318−7327.
5. Zhou, K.; Chen, B. X.; Zhou, X. T.; et al. Selective Synthesis of Furfurylamine by Reductive Amination of Furfural over Raney Co. *ChemCatChem.* **2019**, *11*(22), 5562-5569.