Supplementary Material

Towards the Efficient Catalytic Valorization of Chitin to *N*-Acylethanolamine over Ni/CeO_2 Catalyst: Exploring the Shape-Selective Reactivity

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Additional Discussion Section: Computational Analysis

To further understand the role of Ni in Ni/CeO_2 catalyst, the single-atom Ni was introduced into the (110) surfaces of CeO_2, and the introduced Ni was tightly bonded by four planar oxygen atoms, and four short Ni-O bonds of 1.90 Å are smaller than the covalent radius of 1.94 Å as displayed in Figure S6a-7b, which indicated the coordination nature of these Ni-O bonds as indicated by the obvious increasing electronic localization function (ELF) value between Ni and O in Figure S6c-7d. Moreover, the introduced Ni would significantly influence the charge distribution of the atoms on CeO_2 (110) surface, the introduced Ni reveal the stronger Lewis acidity as indicated by the more positive Bader charge (+2.30 *e*) than Ce (+2.00 *e*), and the catalytic activity would be enhanced along with the introduction of the stronger Lewis acidity. Therefore, the single atom/site-type Ni should be the ideal active site of Ni/CeO_2 (110) to convert chitin to *N*-Acylethanolamine.

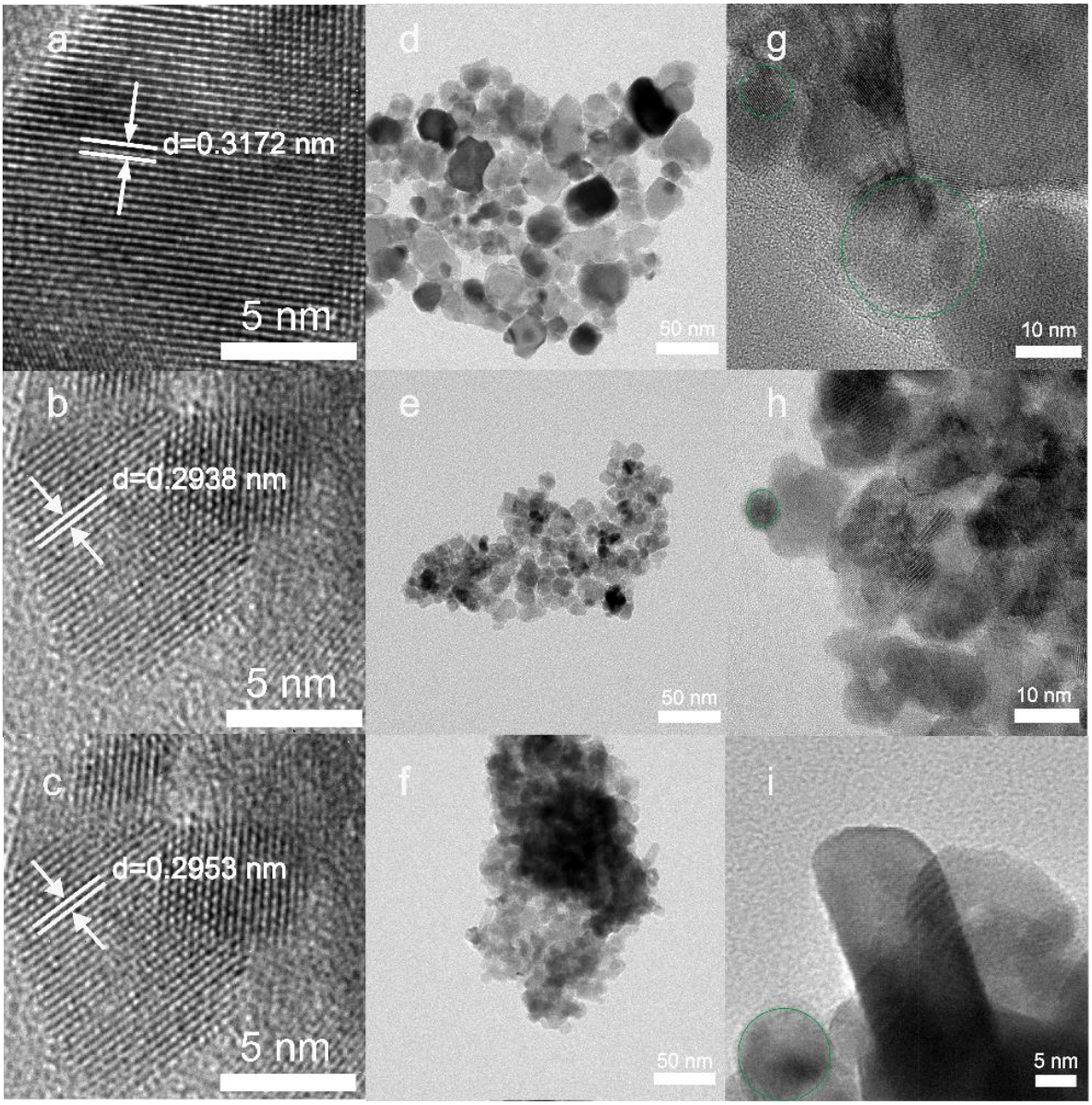


Figure S1. HRTEM images of standalone (**a**) CeO_2 (C), (**b**) CeO_2(P), and (**c**) CeO_2(R) supports and TEM images of three catalysts: (**d**, **g**) Ni/CeO_2(C), (**e**, **h**) Ni/CeO_2(P), and (**f**, **i**) Ni/CeO_2(R).

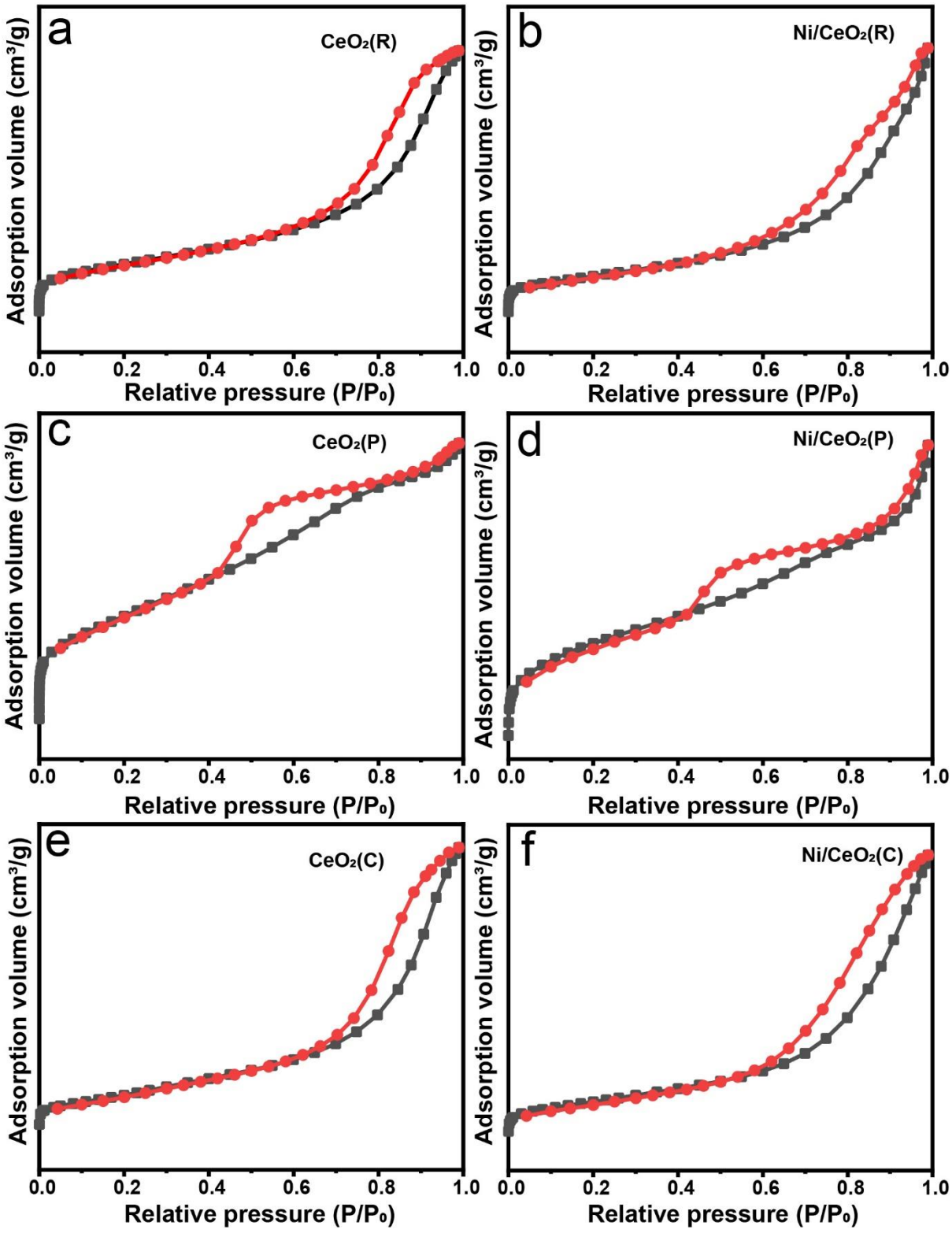


Figure S2. The physical adsorption spectrum of the catalyst. (**a**, **c**, **e**) are the BET spectra of the CeO_2 carrier, respectively; (**b**, **d**, **f**) are the BET spectra of the Ni/CeO_2 catalyst, respectively.

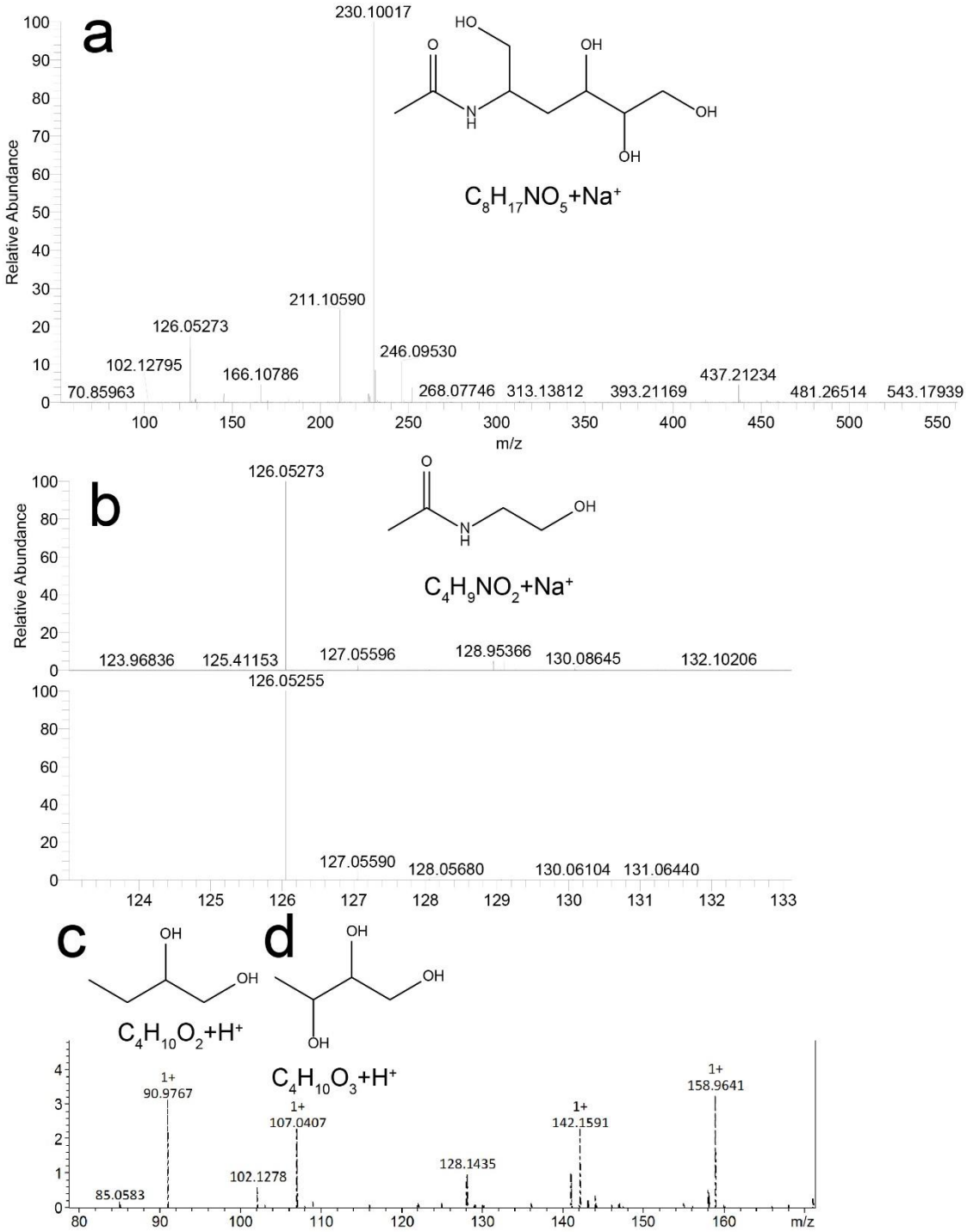


Figure S3. MS spectra of crude reaction mixture: (**a**) N-(1,4,5,6-tetrahydroxyhexan-2-

yl)acetamide, (**b**) *N*-acetylethanolamine, (**c**) butane-1,2-diol and (**d**) butane-1,2,3-triol.

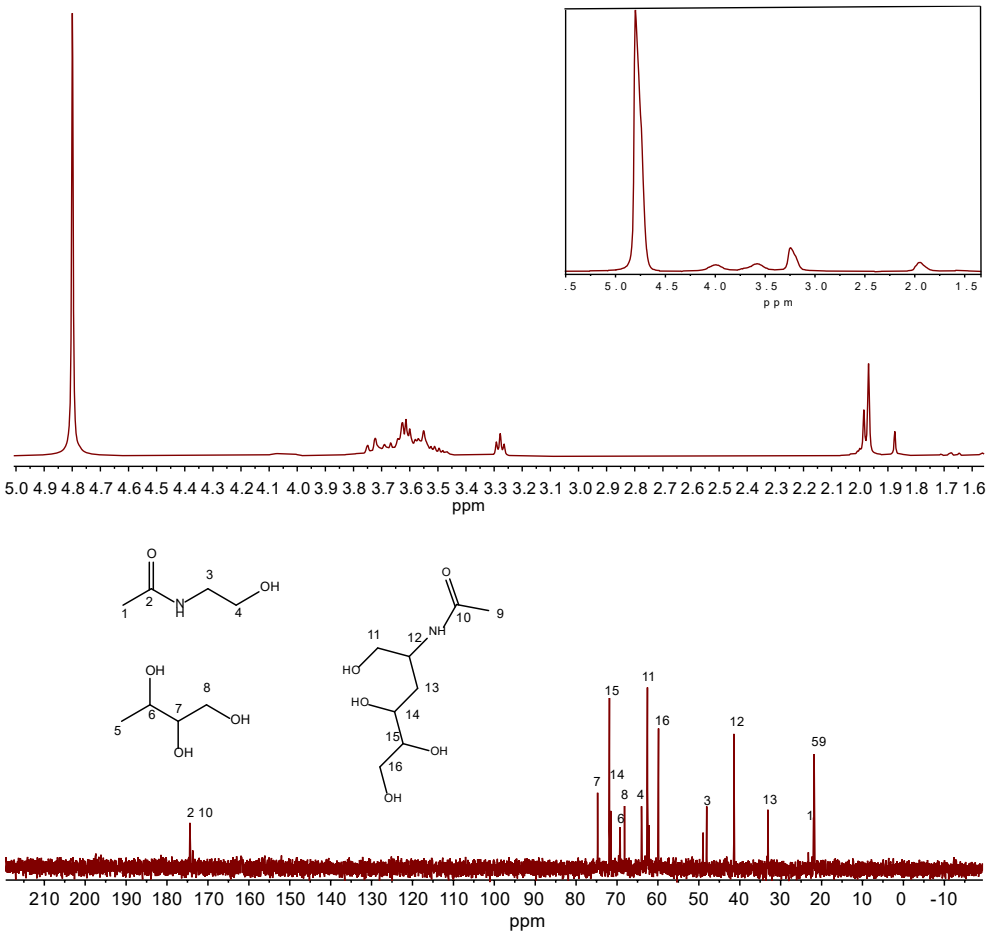


Figure S4. Typical ^{1}H-NMR (top) and ^{13}C-NMR (bottom) spectra of the product after the reaction (Reaction conditions: 1 g NAG, 15 mg catalyst, 5 mL H_2O solvent, 40 bar H_2 pressure, 120 °C temperature, 6 h reaction time). The crude product was not purified. The illustration is ^{2}H-NMR in the inset (Reaction conditions: 1 g NAG, 15 mg catalyst, 5 mL D_2O solvent, 40 bar H_2 pressure), 120 °C temperature, 6 h reaction time).

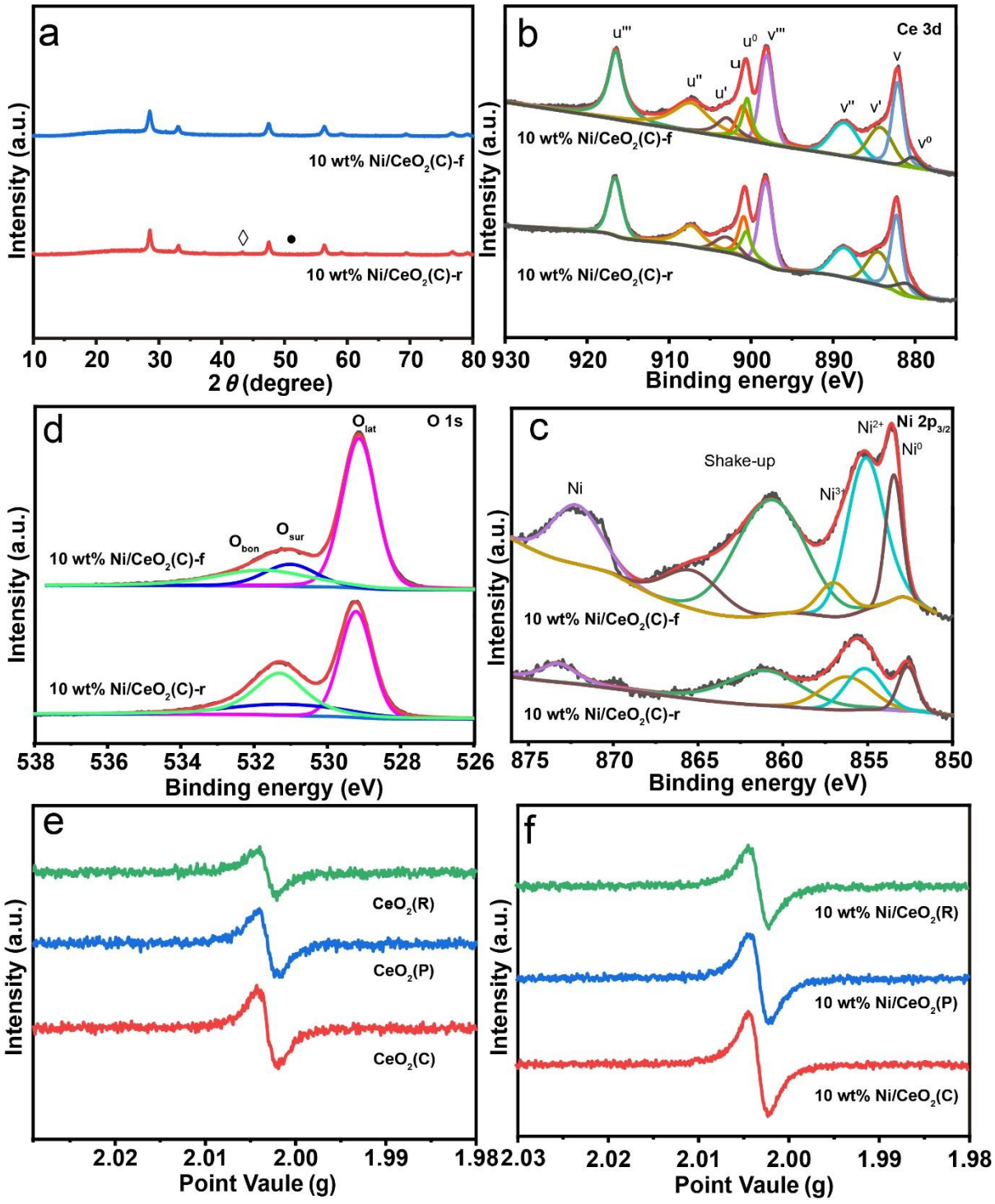


Figure S5. (**a**) XRD patterns and XPS of (**b**) Ce 3d, (**c**) O 1s, and (**d**) Ni 3d spectra of Ni/CeO_2(C)-f, Ni/CeO_2(C)-r catalytic materials.(**e**) and (**f**) EPR spectra of CeO_2(R), CeO_2(P), CeO_2(C) and Ni/CeO_2(R), Ni/CeO_2(P) and Ni/CeO_2(C) catalytic materials.

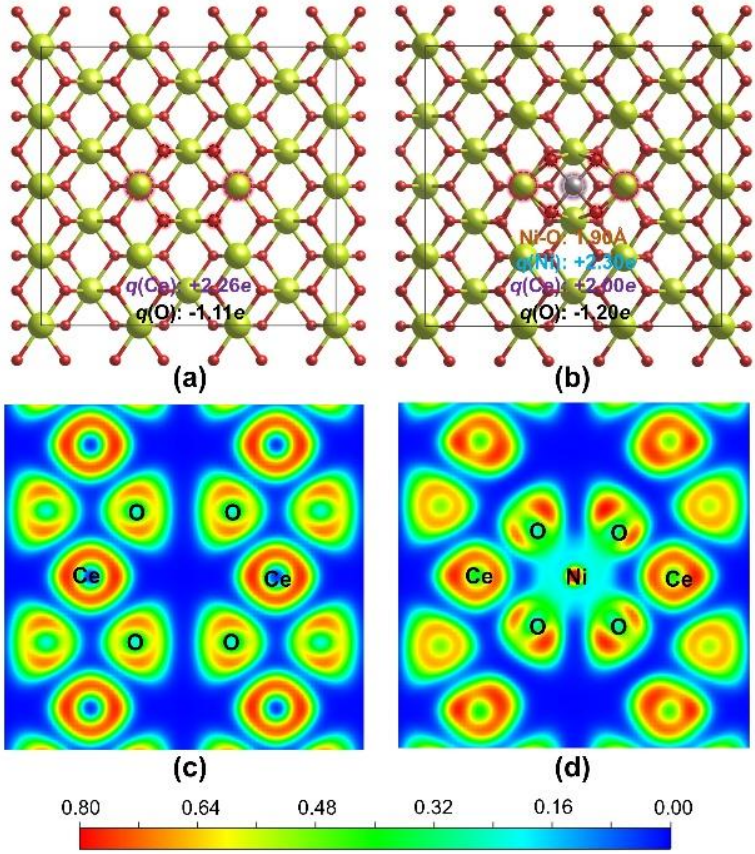
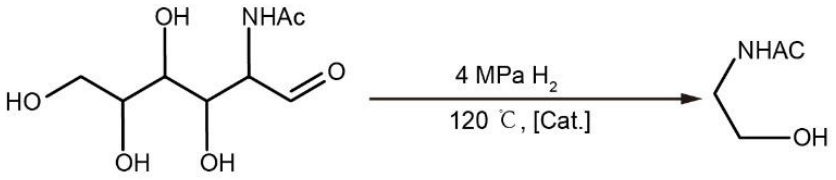


Figure S6. Geometrical structures of (**a**) CeO_2 (110) surface and (**b**) Ni assembled CeO_2 (110) surface. Electronic Localization Function of (**a**) CeO_2 (110) surface and (**b**) Ni assembled CeO_2 (110) surface. Atoms in Green: Ce, red: O, gray: Ni.

Table S1. The catalytic screening: The comparison study.



Glucosamine N-Acetylethanolamine

Cat.	T(h)	*N*-Acetylethanolamine (%)
5 wt% Ru/C	6	13
5 wt% Rh/C	6	28
10 wt% Pd/C	6	16
5 wt% Ru/Al_2O_3	6	29
5 wt% Ni/TiO_2	6	8
10 wt% Ni/ZSM-5	6	10
10 wt% Ni/KIT-6	6	5
10 wt% Ni-4 wt% Ru/CeO_2	6	39
10 wt% Ni/SBA-15	6	27
10 wt% Ni/CeO_2(C) [a]	6	0
10 wt% Ni/CeO_2(C) [b]	6	0

10 wt% Ni/CeO_2(C)	0.5	19
10 wt% Ni/CeO_2(C)	1	36
10 wt% Ni/CeO_2(C)	2	40
10 wt% Ni/CeO_2(C)	4	33
10 wt% Ni/CeO_2(C)	6	38
10 wt% Ni/CeO_2(C)	8	42
10 wt% Ni/CeO_2(R)	0.5	14
10 wt% Ni/CeO_2(R)	1	12
10 wt% Ni/CeO_2(R)	2	14
10 wt% Ni/CeO_2(R)	4	14
10 wt% Ni/CeO_2(R)	6	42
10 wt% Ni/CeO_2(R)	8	34
10 wt% Ni/CeO_2(P)	0.5	25
10 wt% Ni/CeO_2(P)	1	26
10 wt% Ni/CeO_2(P)	2	27
10 wt% Ni/CeO_2(P)	4	29
10 wt% Ni/CeO_2(P)	6	38
10 wt% Ni/CeO_2(P)	8	23

Condition: [a] is 1 bar N_2, [b] is 1 bar air, the yield is quantified by NMR.

Table S2. The representative comparison of catalytic performance of the conversion of *N*-acetylglucosamine to different target products over different catalysts.

Catalyst	**Product**	**Yield (%)**	**Reaction conditions**	**Ref.**
Ru/C	*N*-acetylmonoethanolamine (AMEA)	29	H_2 (4 MPa), $NaHCO_3$, 393K, 1 h	[1]

Ru/C	Acetylglycine (AcGly)	22	1. H_2 (4 MPa), $NaHCO_3$, 393K, 1 h 2. O_2 (1MPa), $NaHCO_3$, 393K, 1 h	[1]
V_2O_5	Acetic acid	33.4	O_2 (0.5 MPa), 2 h, 493K	[2]
[Pyz]Cl	3-acetylamino-5-acetylfuran	36.9	463K, 1 h	[3]
H_2SO_4	levulinic acid	20.6	463K, 10 min	[4]
1-methyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate	levulinic acid	67	180 °C, 5 h, 1 g $[C_3SO_3Hmim]HSO_4$,6 g of H_2O	[5]
Ni/CeO_2	*N*-acetylmonoethanolamine (AMEA)	42	H_2 (4 MPa), $NaHCO_3$, 393K, 6 h	This work

Table S3. Several CeO_2 sample conditions.

Entry	m NaOH (g)	T (°C)	Shape
1	0.96	100	CeO_2(R)
2	0.016	100	CeO_2(P)
3	0.96	180	CeO_2(C)

References

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