# Supporting Information

# A synergistic strategy of hierarchical pore engineering and ligand functionalization: Modulating Ni sites in Ce-UiO-66 for dicyclopentadiene hydrogenation under mild conditions

Yunqi Zhang, Tianyu Zhang, Yifei Ye, Xinmeng Xu, Wenjuan Xiang, Xiubing Huang*, Ge Wang*

Beijing Key Laboratory of Function Materials for Molecule & Structure Construction, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, PR China

* Corresponding authors: xiubinghuang@ustb.edu.cn (X. Huang), gewang@ustb.edu.cn (G. Wang).

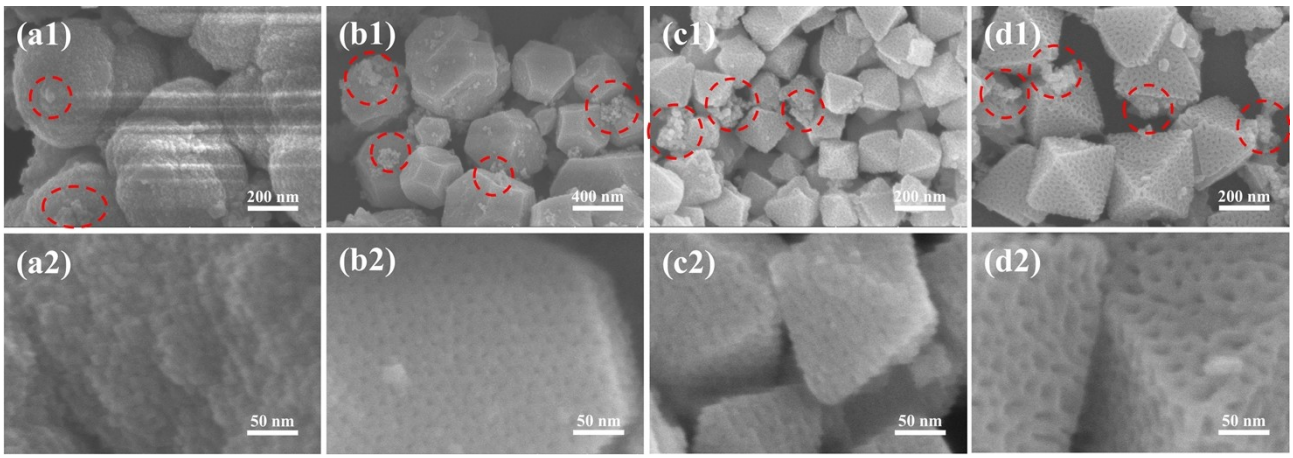


**Fig. S1.** SEM images of (a) 4Ni/HP-U(Ce)-$NH_2$, (b) 4Ni/HP-U(Ce)-H, (c) 4Ni/HP-U(Ce)-$NO_2$, (d) 4Ni/HP-U(Ce)-Br (10-0).

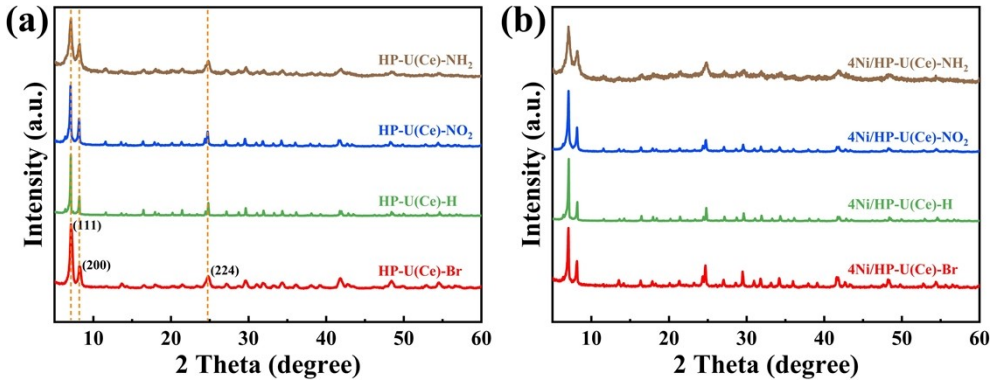


**Fig. S2.** XRD patterns of (a) HP-U(Ce)-X, (b) 4Ni/HP-U(Ce)-X.

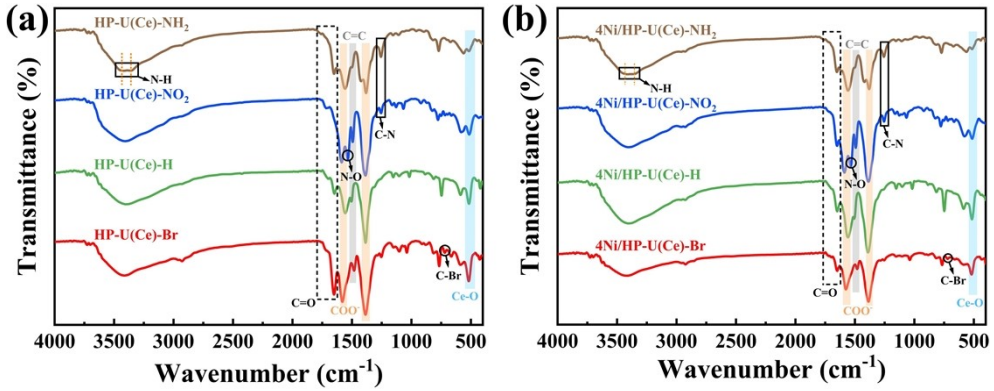


**Fig. S3.** FT-IR spectra of (a) HP-U(Ce)-X, (b) 4Ni/HP-U(Ce)-X.

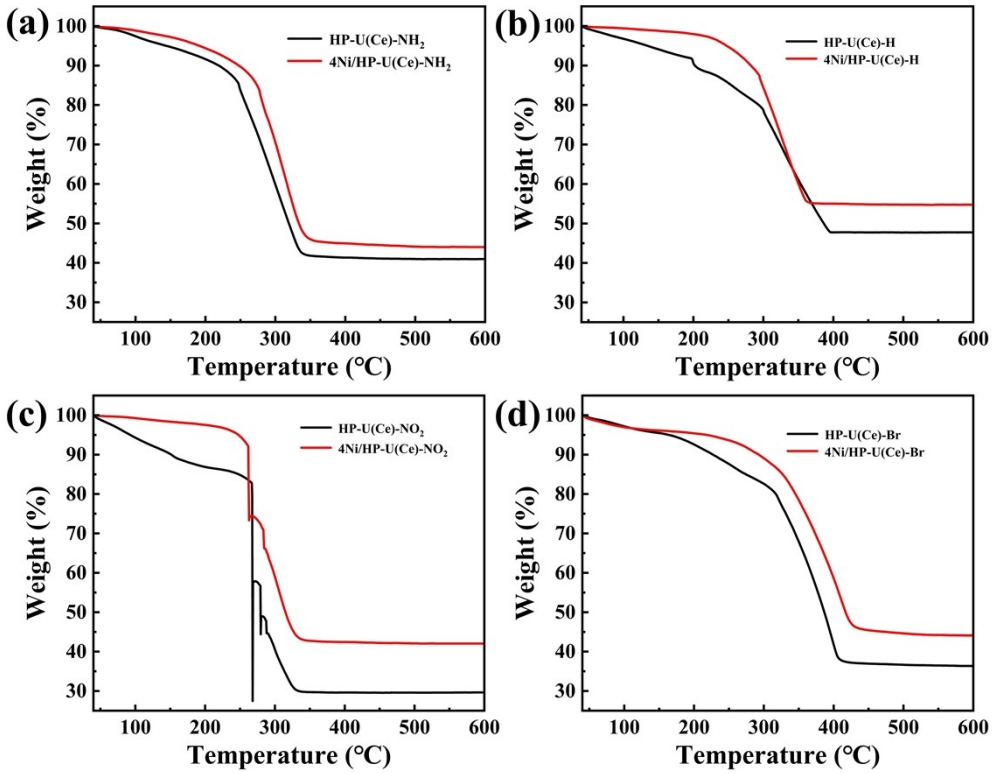


**Fig. S4.** TG curves of (a) HP-U(Ce)-$NH_2$, (b) HP-U(Ce)-H, (c) HP-U(Ce)-$NO_2$, (d) HP-U(Ce)-Br (10-0) and corresponding Ni-loaded samples.

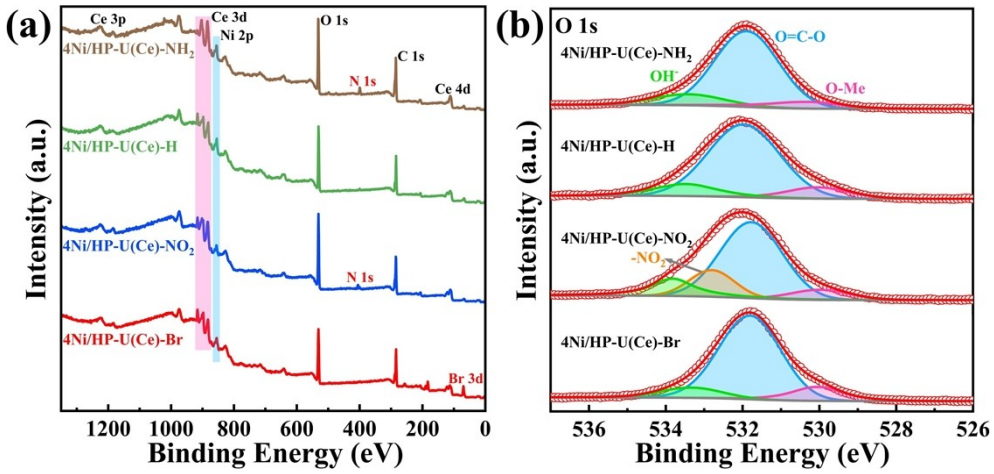


**Fig. S5.** (a) Full survey and (b) O 1s XPS spectra of 4Ni/HP-U(Ce)-X.

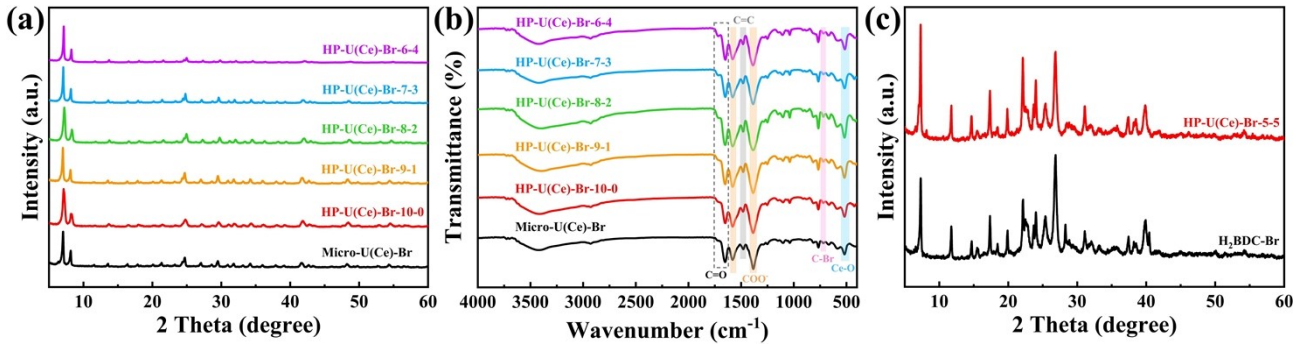


**Fig. S6.** (a) XRD patterns and (b) FT-IR spectra of Micro-U(Ce)-Br and HP-U(Ce)-Br-*x*-*y*.

(c) XRD pattern of HP-U(Ce)-Br-5-5.

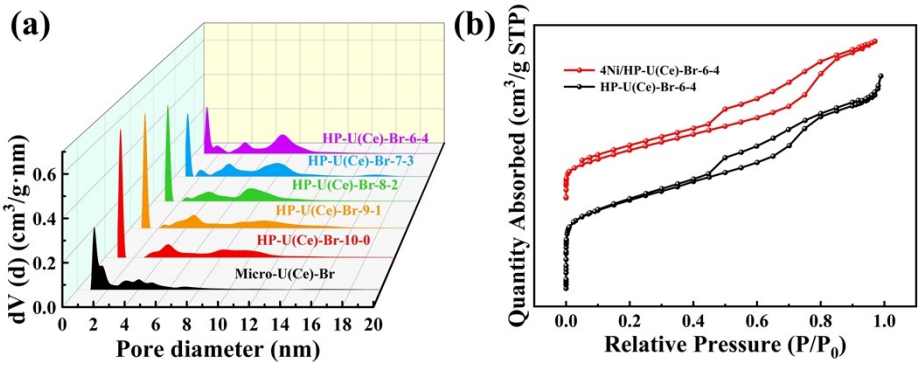


**Fig. S7.** (a) Pore size distributions of Micro-U(Ce)-Br and HP-U(Ce)-Br-*x*-*y*,

(b) $N_2$ adsorption-desorption isotherm of 4Ni/HP-U(Ce)-Br-6-4

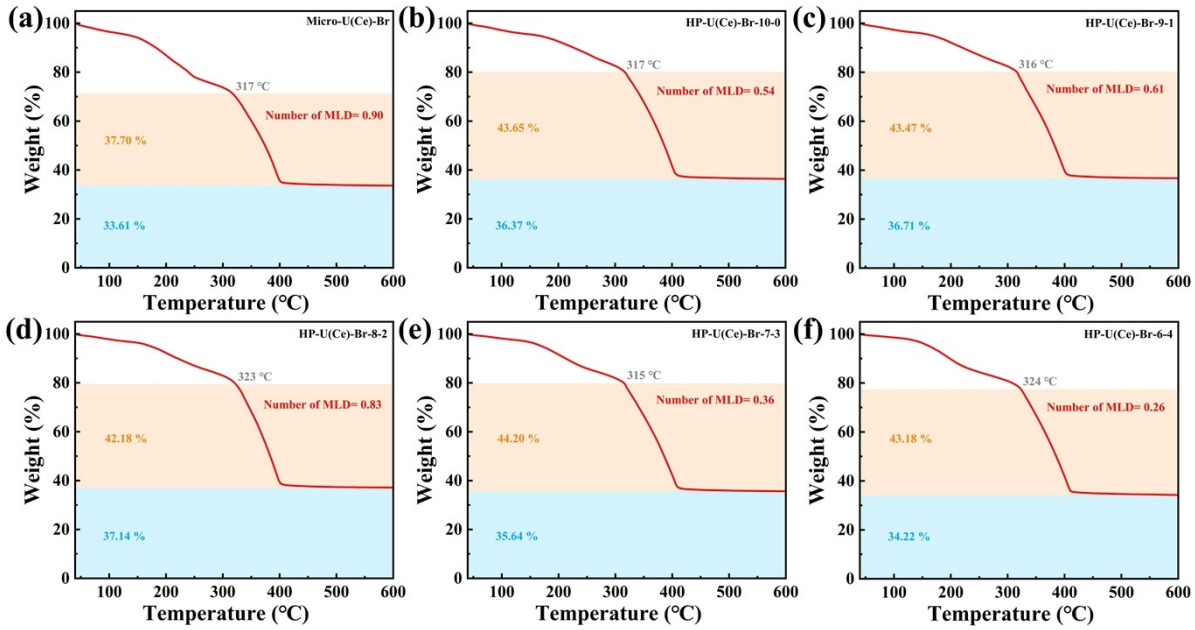


**Fig. S8.** TG curves of (a) Micro-U(Ce)-Br, (b) HP-U(Ce)-Br-10-0, (c) HP-U(Ce)-Br-9-1,

(d) HP-U(Ce)-Br-8-2, (e) HP-U(Ce)-Br-7-3, (f) HP-U(Ce)-Br-6-4.

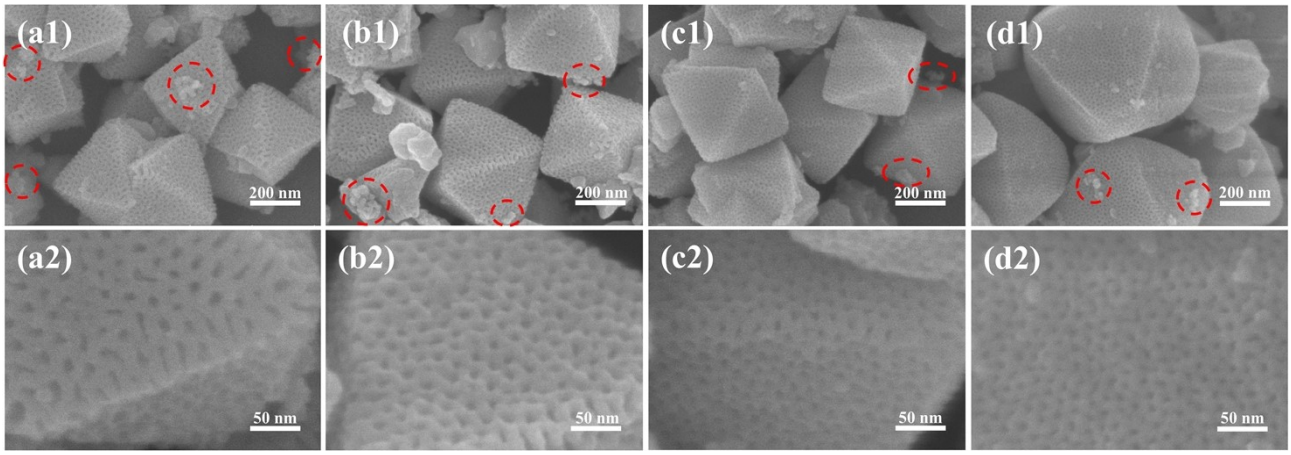


**Fig. S9.** SEM images of (a) 4Ni/HP-U(Ce)-Br-9-1, (b) 4Ni/HP-U(Ce)-Br-8-2, (c) 4Ni/HP-U(Ce)-Br-7-3, (d) 4Ni/HP-U(Ce)-Br-6-4.

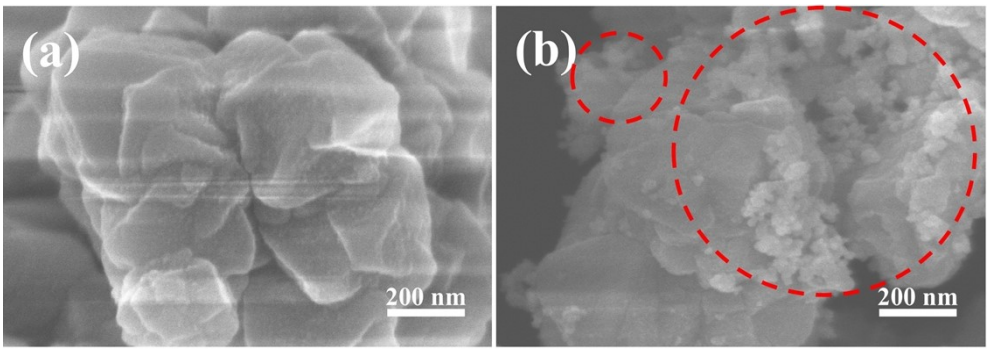


**Fig. S10.** SEM images of (a) Micro-U(Ce)-Br and (b) 4Ni/Micro-U(Ce)-Br.

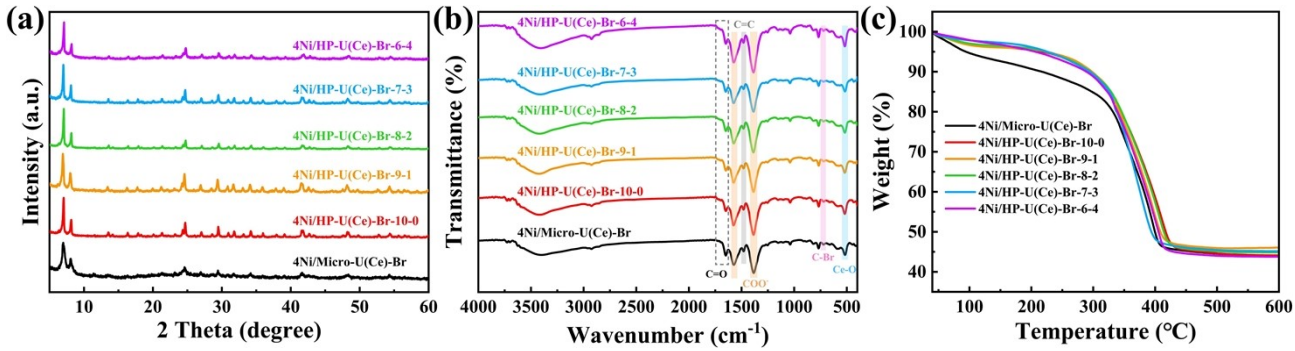


**Fig. S11.** (a) XRD patterns, (b) FT-IR spectra and (c) TG curves of 4Ni/Micro-U(Ce)-Br and 4Ni/HP-U(Ce)-Br-*x*-*y*.

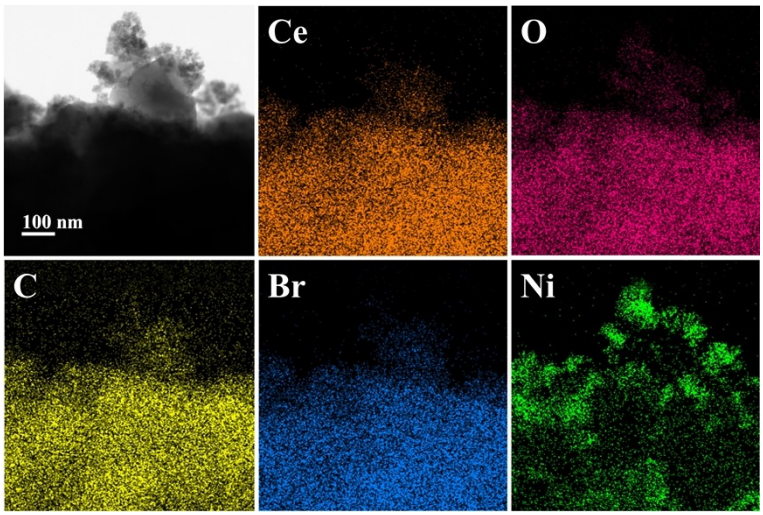


**Fig. S12.** HAADF-STEM image with EDX elemental mapping images of 4Ni/Micro-U(Ce)-Br.

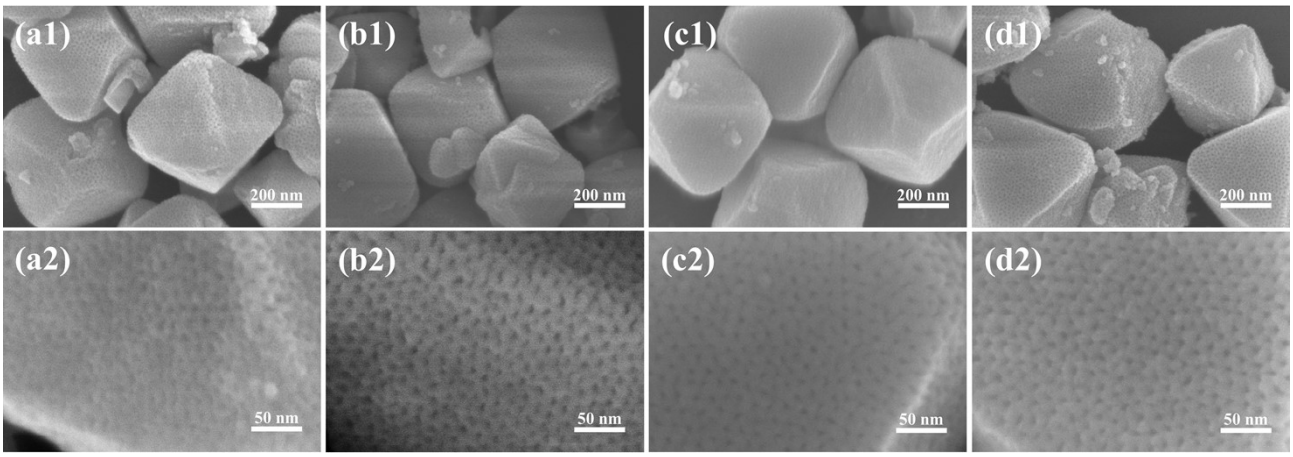


**Fig. S13.** SEM images of (a) 1Ni/HP-U(Ce)-Br-6-4, (b) 2Ni/HP-U(Ce)-Br-6-4, (c) 3Ni/HP-U(Ce)-Br-6-4, (d) 5Ni/HP-U(Ce)-Br-6-4.

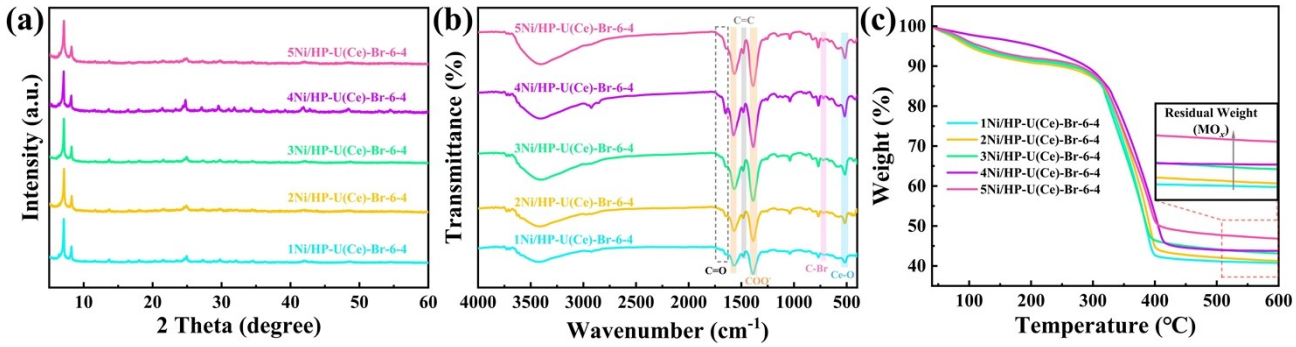


**Fig. S14.** (a) XRD patterns, (b) FT-IR spectra and (c) TG curves of *z*Ni/HP-U(Ce)-Br-6-4.

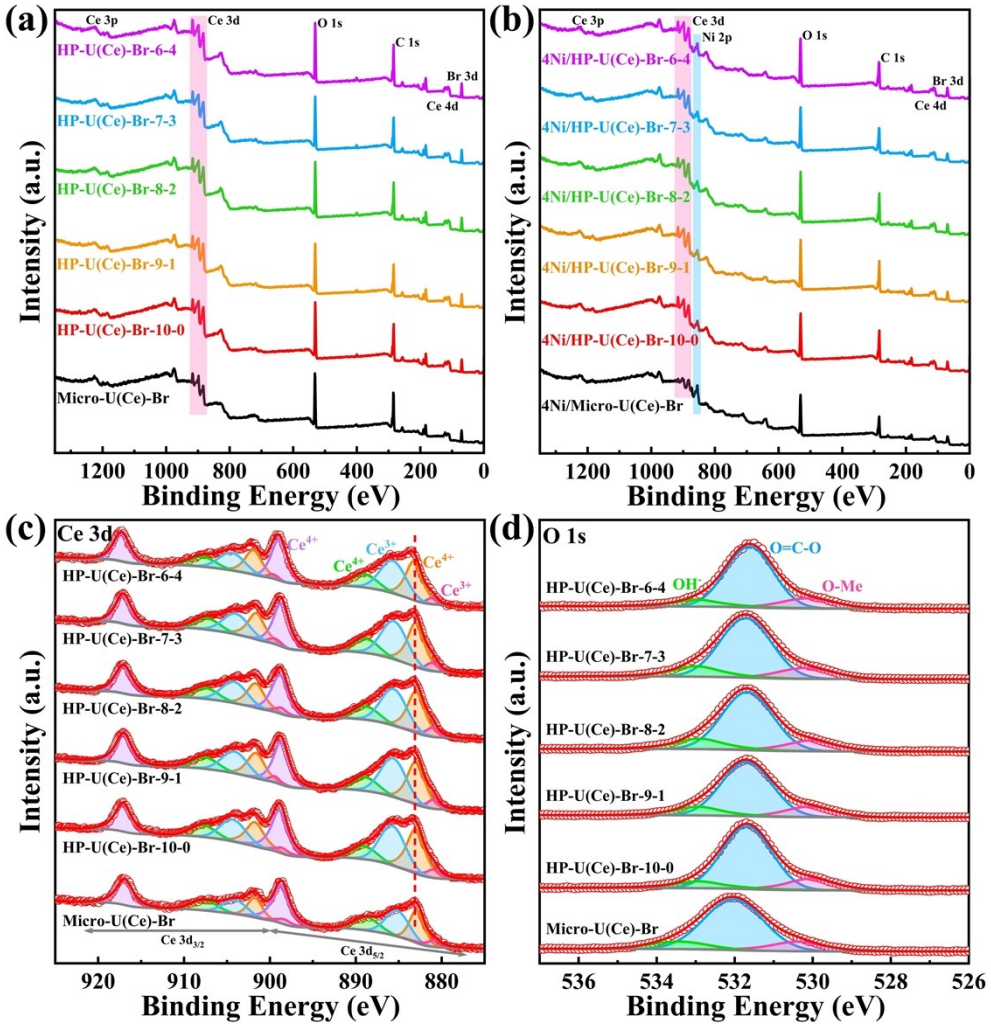


**Fig. S15.** Full survey XPS spectra of (a) Micro-U(Ce)-Br and HP-U(Ce)-Br-*x*-*y*, (b) 4Ni/Micro-U(Ce)-Br and 4Ni/HP-U(Ce)-Br-*x*-*y*. (c) Ce 3d, (d) O 1s XPS spectra of Micro-U(Ce)-Br and HP-U(Ce)-Br-*x*-*y*.

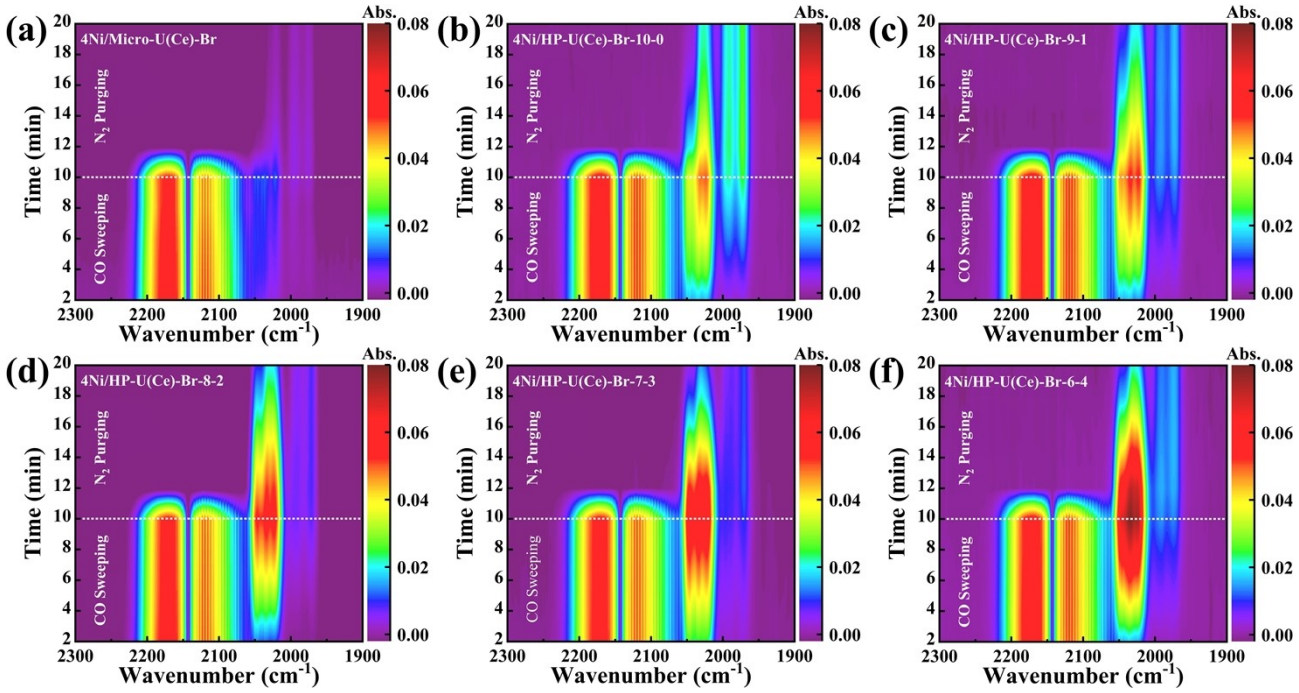


**Fig. S16.** In-situ CO-DRIFTS spectra of (a) 4Ni/Micro-U(Ce)-Br, (b) 4Ni/HP-U(Ce)-Br-10-0, (c) 4Ni/HP-U(Ce)-Br-9-1, (d) 4Ni/HP-U(Ce)-Br-8-2, (e) 4Ni/HP-U(Ce)-Br-7-3, (f) 4Ni/HP-U(Ce)-Br-6-4.

**Table S1.** Pore parameters from nitrogen sorption isotherms of samples.

| Samples | $A_{BET}$ ($m^2/g$) | $V_{total}$ ($cm^3/g$) | $A_{micro.}$ ($m^2/g$) | $V_{micro.}$ ($cm^3/g$) | $A_{meso.}$ ($m^2/g$) | $V_{meso.}$ ($cm^3/g$) |
|---|---|---|---|---|---|---|
| **HP-U(Ce)-$NH_2$** | 410.15 | 1.039 | 133.96 | 0.127 | 276.19 | 0.912 |
| **HP-U(Ce)-H** | 1344.95 | 0.998 | 876.08 | 0.377 | 468.87 | 0.621 |
| **HP-U(Ce)-$NO_2$** | 1088.12 | 1.068 | 570.18 | 0.256 | 517.94 | 0.812 |
| **Micro-U(Ce)-Br** | 581.66 | 0.401 | 410.38 | 0.190 | 171.28 | 0.211 |
| **HP-U(Ce)-Br (10-0)** | 704.68 | 0.618 | 429.62 | 0.190 | 275.06 | 0.428 |
| **HP-U(Ce)-Br-9-1** | 728.71 | 0.648 | 412.31 | 0.183 | 316.40 | 0.465 |
| **HP-U(Ce)-Br-8-2** | 691.08 | 0.611 | 409.54 | 0.187 | 281.54 | 0.424 |
| **HP-U(Ce)-Br-7-3** | 637.09 | 0.640 | 315.97 | 0.154 | 321.12 | 0.486 |
| **HP-U(Ce)-Br-6-4** | 621.69 | 0.641 | 282.22 | 0.134 | 339.47 | 0.507 |
| **4Ni/HP-U(Ce)-Br-6-4** | 233.42 | 0.311 | 53.02 | 0.029 | 180.40 | 0.282 |

$A_{BET}$ is the Brunauer-Emmett-Teller (BET) specific surface area

$V_{total}$ is the total pore volume calculated by the single point adsorption at $P/P_0$ =0.99

$A_{micro.}$ is the specific micropore surface area calculated by t-plot analysis

$V_{micro.}$ is the micropore volume calculated by t-plot analysis

$A_{meso.}$ is the specific mesopore surface area emtimated by subtracting $A_{micro.}$ from $A_{BET}$

$V_{meso.}$ is the mesopore volume emtimated by subtracting $V_{micro.}$ from $V_{total}$

**Table S2.** XPS quantitative analysis of Ce 3d, O 1s, and Ni 2p derived from the area ratio of peaks.

| Samples | $Ce^{3+}/(Ce^{4+}+Ce^{3+})$ | $O_{ads.}/O_{total}$ | $Ni^{0}/(Ni^{0}+Ni^{2+})$ |
|---|---|---|---|
| **4Ni/HP-U(Ce)-$NH_2$** | 53.59% | 12.92% | 12.70% |
| **4Ni/HP-U(Ce)-H** | 30.99% | 12.45% | 22.53% |
| **4Ni/HP-U(Ce)-$NO_2$** | 42.94% | 13.85% | 15.33% |
| **4Ni/HP-U(Ce)-Br (10-0)** | 36.78% | 10.98% | 25.17% |
| **4Ni/HP-U(Ce)-Br-9-1** | 36.43% | 12.07% | 24.49% |
| **4Ni/HP-U(Ce)-Br-8-2** | 40.13% | 12.33% | 28.88% |
| **4Ni/HP-U(Ce)-Br-7-3** | 41.70% | 11.87% | 34.31% |
| **4Ni/HP-U(Ce)-Br-6-4** | 44.52% | 10.56% | 27.60% |
| **4Ni/Micro-U(Ce)-Br** | 36.83% | 12.25% | 24.76% |
| **HP-U(Ce)-Br-10-0** | 35.02% | 11.43% | - |
| **HP-U(Ce)-Br-9-1** | 36.14% | 12.49% | - |
| **HP-U(Ce)-Br-8-2** | 38.01% | 14.33% | - |
| **HP-U(Ce)-Br-7-3** | 35.71% | 13.87% | - |
| **HP-U(Ce)-Br-6-4** | 31.54% | 11.83% | - |
| **Micro-U(Ce)-Br** | 30.32% | 12.79% | - |

**Table S3.** Ni content of catalysts from ICP-MS results.

| Catalysts | Theoretical loading (wt.%) | Experimental loading (wt.%) |
|---|---|---|
| **4Ni/HP-U(Ce)-$NH_2$** | 4 | 4.123 |
| **4Ni/HP-U(Ce)-H** | 4 | 3.867 |
| **4Ni/HP-U(Ce)-$NO_2$** | 4 | 3.947 |
| **4Ni/HP-U(Ce)-Br (10-0)** | 4 | 3.817 |
| **4Ni/HP-U(Ce)-Br-9-1** | 4 | 3.578 |
| **4Ni/HP-U(Ce)-Br-8-2** | 4 | 3.826 |
| **4Ni/HP-U(Ce)-Br-7-3** | 4 | 4.069 |
| **4Ni/HP-U(Ce)-Br-6-4** | 4 | 3.912 |
| **4Ni/HP-U(Ce)-Br-6-4-cycle** | 4 | 3.663 |
| **1Ni/HP-U(Ce)-Br-6-4** | 1 | 1.028 |
| **2Ni/HP-U(Ce)-Br-6-4** | 2 | 2.152 |
| **3Ni/HP-U(Ce)-Br-6-4** | 3 | 3.395 |
| **5Ni/HP-U(Ce)-Br-6-4** | 5 | 5.917 |
| **4Ni/Micro-U(Ce)-Br** | 4 | 3.968 |

**Table S4.** DCPD hydrogenation performance of the reported catalysts.

| Catalysts | Hydrogenation conditions | DCPD Conversion (%) | THDCPD Selectivity (%) | References |
|---|---|---|---|---|
| **Ni-NSs@MSNSs** | 150 ℃, 2.5 MPa, 2 h | >99.5 | 98.9 | [1] |
| **$NiMo_{0.2}/\gamma$-$Al_2O_3$** | 150 ℃, 3.5 MPa, 3 h | 97 | 99.7 | [2] |
| **Ni/SBA-15** | 130 ℃, 2 MPa, 5 h | 70 | 74.8 | [3] |
| **$SiO_2$@Ni/C** | 60-90 ℃, 3 MPa, WHSV= 2 $h^{-1}$, 144 h | 100 | >90 | [4] |
| **Ni@C/g-$C_3N_4$** | 30 ℃, 0.1 MPa, 2 h | >99.9 | >99.9 | [5] |
| **NiM-2** | 60 ℃, 3 MPa, 0.5 h | 100 | 99.1 | [6] |
| **Ni-53-500** | 60℃, 3MPa, 2 h | 100 | >98 | [7] |
| **MET-1000** | 120 ℃, 3 MPa, 12 h | 100 | >99.9 | [8] |
| **Ru@Meso-UiO-25-200** | 60 ℃, 2 MPa, 0.58 h | 100 | ~100 | [9] |
| **$Ru_1Ni_{1.5}$@UiO-66(Ce)-12 h** | 35 ℃, 1 MPa, 0.42 h | 100 | ~100 | [10] |
| **Pt NCs@Ce-PyDC-3** | 50 ℃, 1 MPa, 1 h | 100 | 99 | [11] |
| **Pd/UiO-67(Ce)-bpy** | 70 ℃, 1 MPa, 1 h | >99 | 96.4 | [12] |
| **Ir@Ce-UiO-66-$NO_2$** | 70 ℃, 2 MPa, 2 h | 100 | >99 | [13] |
| **Ni/La NPs@UD** | 70 ℃, 1 MPa, 1.5 h | 100 | 99.9 | [14] |
| **$Ni_5$@U(Ce)-40eq-5** | 70 ℃, 2 MPa, 1.5 h | 100 | 100 | [15] |
| **3Ni/HP-UiO-66** | 100 ℃, 2 MPa, 1 h | 100 | >99.9 | [16] |
| **5Ni/Ce-UiO-2HAc** | 100 ℃, 2 MPa, 0.83 h | 100 | ~100 | [17] |
| **Ni/Ce-UiO-66-Br** | 100 ℃, 2 MPa, 3 h | 100 | 100 | [18] |
| **4Ni/HP-U(Ce)-Br-6-4** | 60 ℃, 2 MPa, 0.5 h | 100 | 95 | This work |
| | 70 ℃, 2 MPa, 0.5 h | 100 | ~100 | |

**Table S5.** $H_2$-TPD data of the catalysts.

| Catalysts | Total adsorption quantity of $H_2$ (mmol/g) | Peak concentration (%) |
|---|---|---|
| **1Ni/HP-U(Ce)-Br-6-4** | 0.2852 | 0.04 |
| **2Ni/HP-U(Ce)-Br-6-4** | 0.3166 | 0.05 |
| **3Ni/HP-U(Ce)-Br-6-4** | 0.3345 | 0.05 |
| **4Ni/HP-U(Ce)-Br-6-4** | 0.4287 | 0.06 |
| **5Ni/HP-U(Ce)-Br-6-4** | 0.3814 | 0.08 |
| **4Ni/HP-U(Ce)-Br-10-0** | 0.4385 | 0.08 |
| **4Ni/HP-U(Ce)-Br-9-1** | 0.4488 | 0.08 |
| **4Ni/HP-U(Ce)-Br-8-2** | 0.4361 | 0.09 |
| **4Ni/HP-U(Ce)-Br-7-3** | 0.4059 | 0.09 |
| **4Ni/Micro-U(Ce)-Br** | 0.3141 | 0.07 |

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