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Electronic Supplementary Information (ESI) for

A General and Selective Ni-Catalysed Reductive Amination using Hydrazine Hydrate as Facile Nitrogen and Hydrogen Sources

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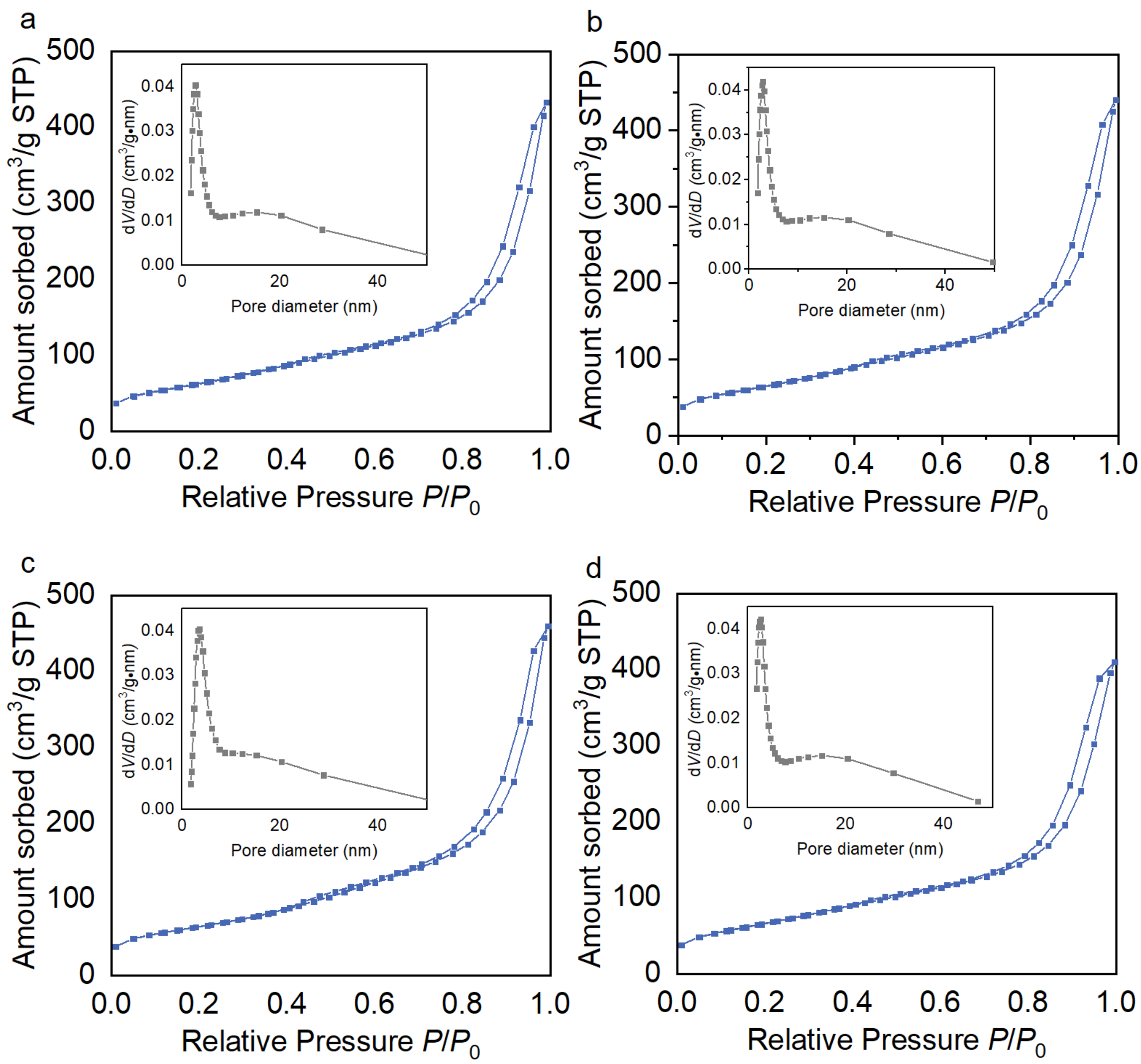


Figure S1. N_2 adsorption-desorption isotherms and the BJH pore size distrubution (inset) of (a) Ni/*meso*-Al_2O_3-400; (b) Ni/*meso*-Al_2O_3-500; (c) Ni/*meso*-Al_2O_3-600; (d) Ni/*meso*-Al_2O_3-700.

Table S1. Physicochemical properties for various Ni/*meso*-Al_2O_3-*T* catalysts.

Entry	Catalyst	S_{BET} ($m^2 \cdot g^{-1}$)[a]	V_p ($cm^3 \cdot g^{-1}$)[a]	D_p (nm)[a]	Actual Ni loading (wt%)[b]
1	Ni/*meso*-Al_2O_3-400	234	0.669	11	6.50
2	Ni/*meso*-Al_2O_3-500	240	0.679	11	6.60
3	Ni/*meso*-Al_2O_3-600	231	0.686	11	6.62
4	Ni/*meso*-Al_2O_3-700	246	0.607	10	6.79

[a] Specific surface area (S_{BET}), cumulative pore volume (V_p), and pore diameter (D_p) were determined by N_2 physisorption. [b] Actual Ni loadings were deterimined by ICP-OES.

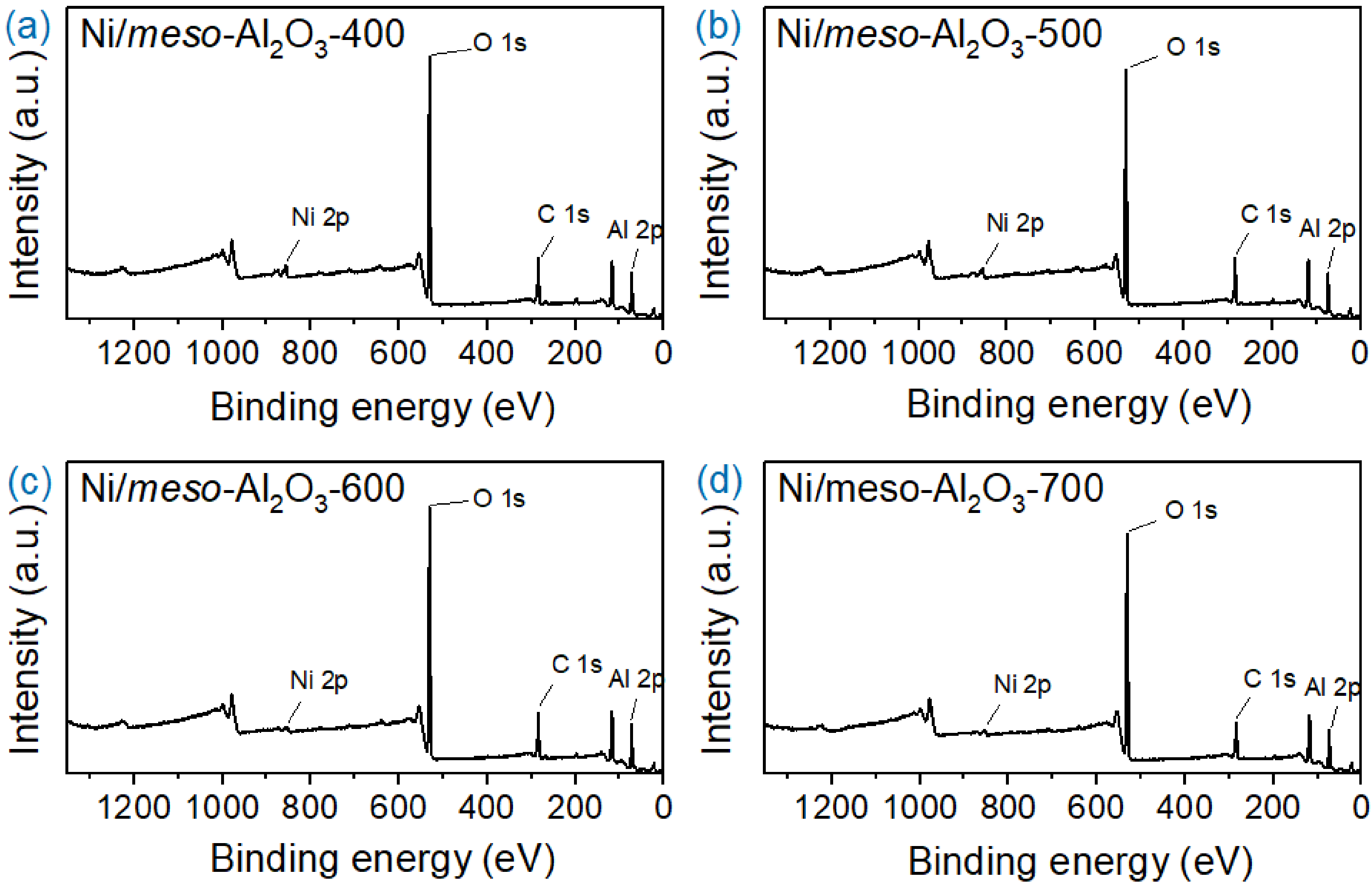


Figure S2. Full-scan XPS spectrum of (a) Ni/*meso*-Al_2O_3-400; (b) Ni/*meso*-Al_2O_3-500; (c) Ni/*meso*-Al_2O_3-600; (d) Ni/*meso*-Al_2O_3-700.

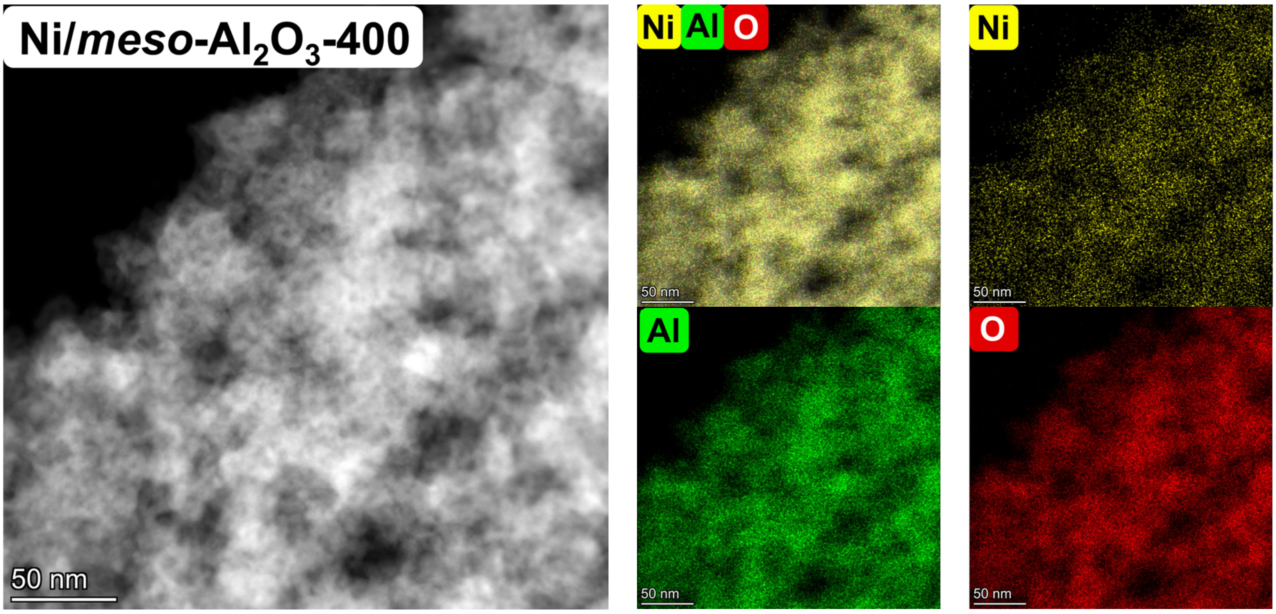


Figure S3. HAADF-STEM image and representative EDS elemental maps of nickel (yellow), alumina (green), and oxygen (red) for Ni/*meso*-Al_2O_3-400.

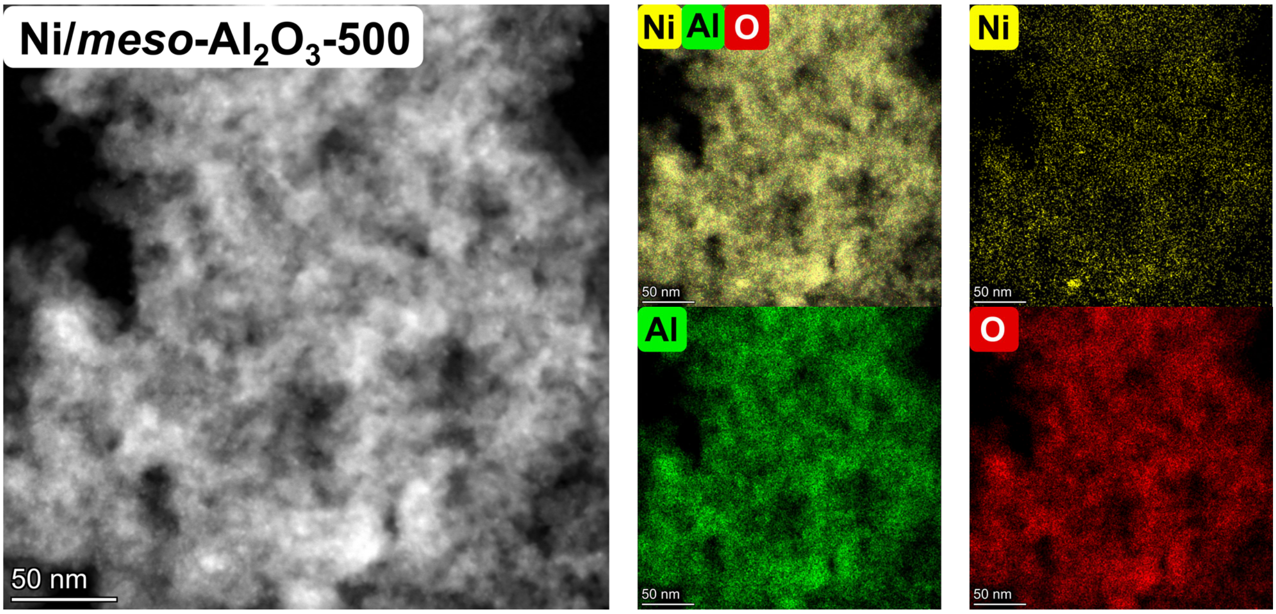


Figure S4. HAADF-STEM image and representative EDS elemental maps of nickel (yellow), alumina (green), and oxygen (red) for Ni/*meso*-Al_2O_3-500.

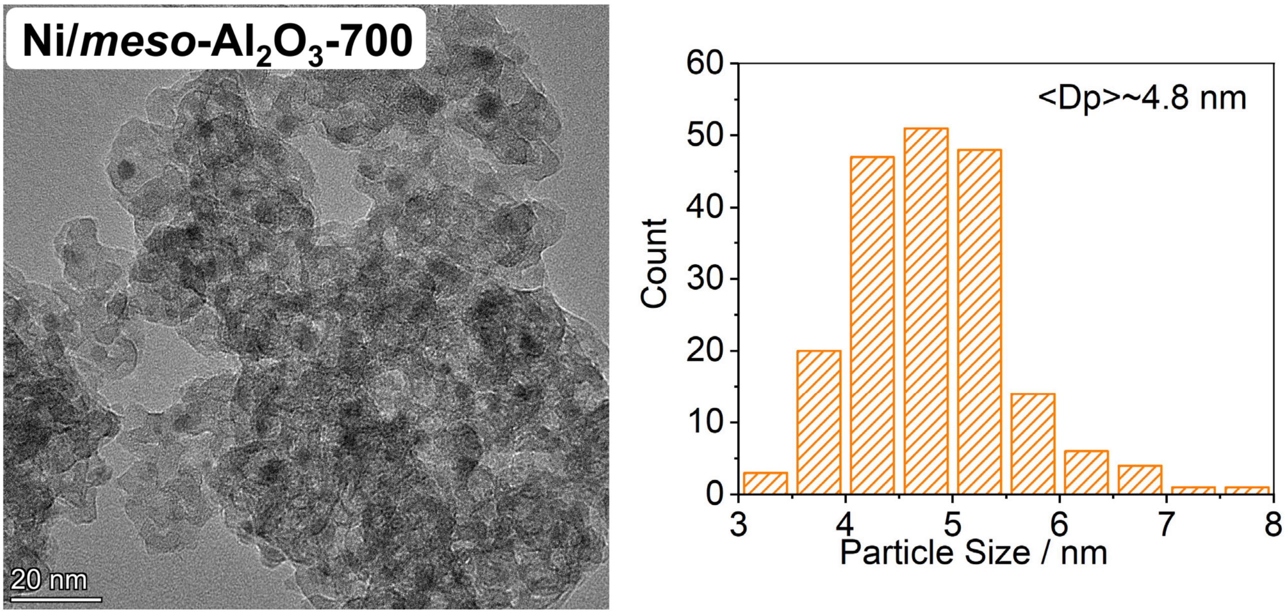


Figure S5. TEM image and Ni particle size distribution of Ni/*meso*-Al_2O_3-700.

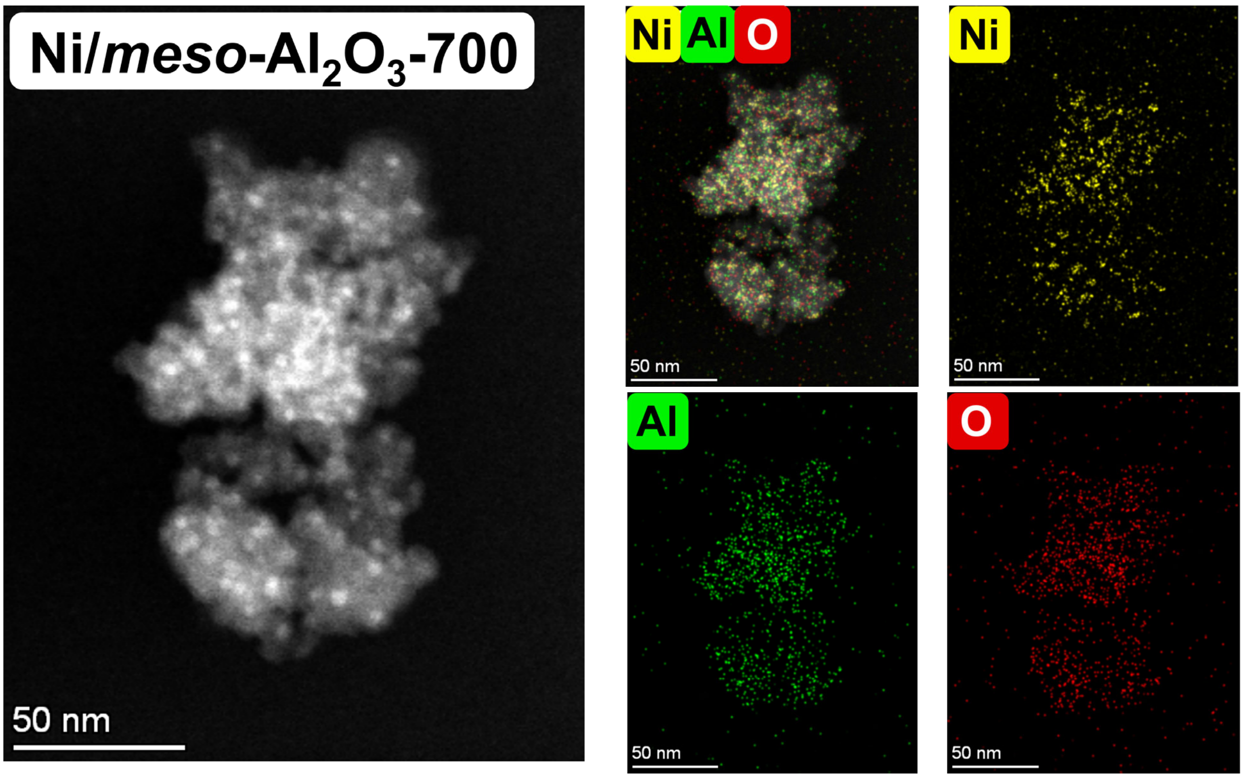
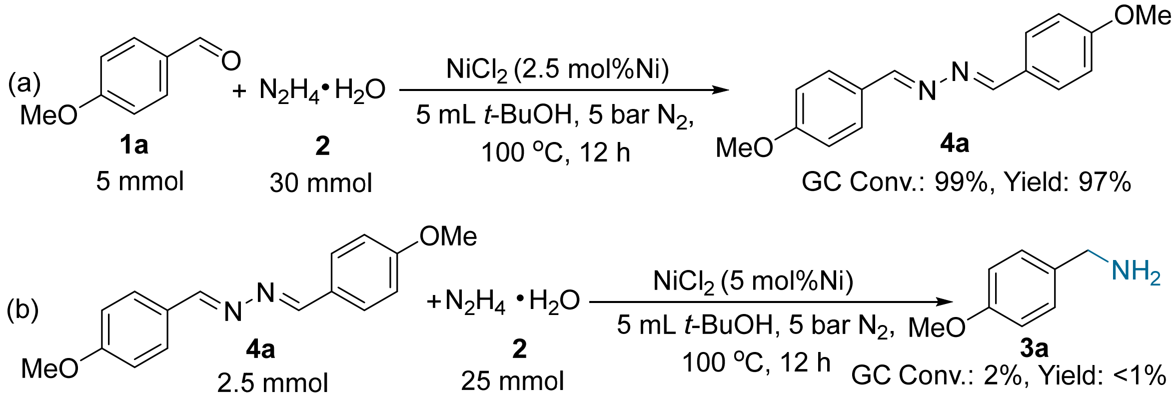
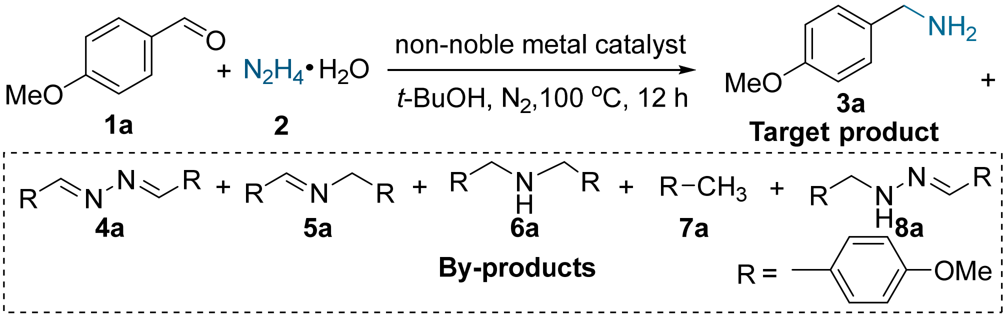


Figure S6. HAADF-STEM image and representative EDS elemental maps of nickel (yellow), alumina (green), and oxygen (red) for Ni/*meso*-Al_2O_3-700.



Scheme S1. Control experiments for the reactions of **1a** and **4a** in the presence of $NiCl_2$.

***Table S2*.** Reductive amination of 4-methoxybenzyl aldehyde (**1a**) with hydrazine hydrate (**2**) over different catalysts.[a]



Entry	Catalyst	Conv. (%)	Yield (%)[b]					
			3a	4a	5a	6a	7a	8a
1	Ni/MgO-600	100	**70**	0	8	11	11	0
2	Ni/ZnO-600	100	**51**	10	0	39	0	0
3	Ni/CeO_2-600	100	**17**	83	0	0	0	0
4	Ni/Nb_2O_5-600	100	**16**	82	0	0	0	0
5	Fe/*meso*-Al_2O_3-600	100	**0**	93	1	0	0	6
6	Co/*meso*-Al_2O_3-600	100	**0**	98	0	0	0	1
7	Cu/*meso*-Al_2O_3-600	100	**0**	95	0	0	0	4

[a]Reaction conditions: 4-methoxy benzaldehyde (5.0 mmol), hydrazine hydrate (30 mmol), catalyst (2.5 mol% metal based on **1a**), *t*-BuOH (5.0 mL), 100 °C, 5 bar N_2, 12 h; n.r.=no reaction. [b]Conversions and yields were determined by GC-MS and GC analysis based on the consumption of **1a**.

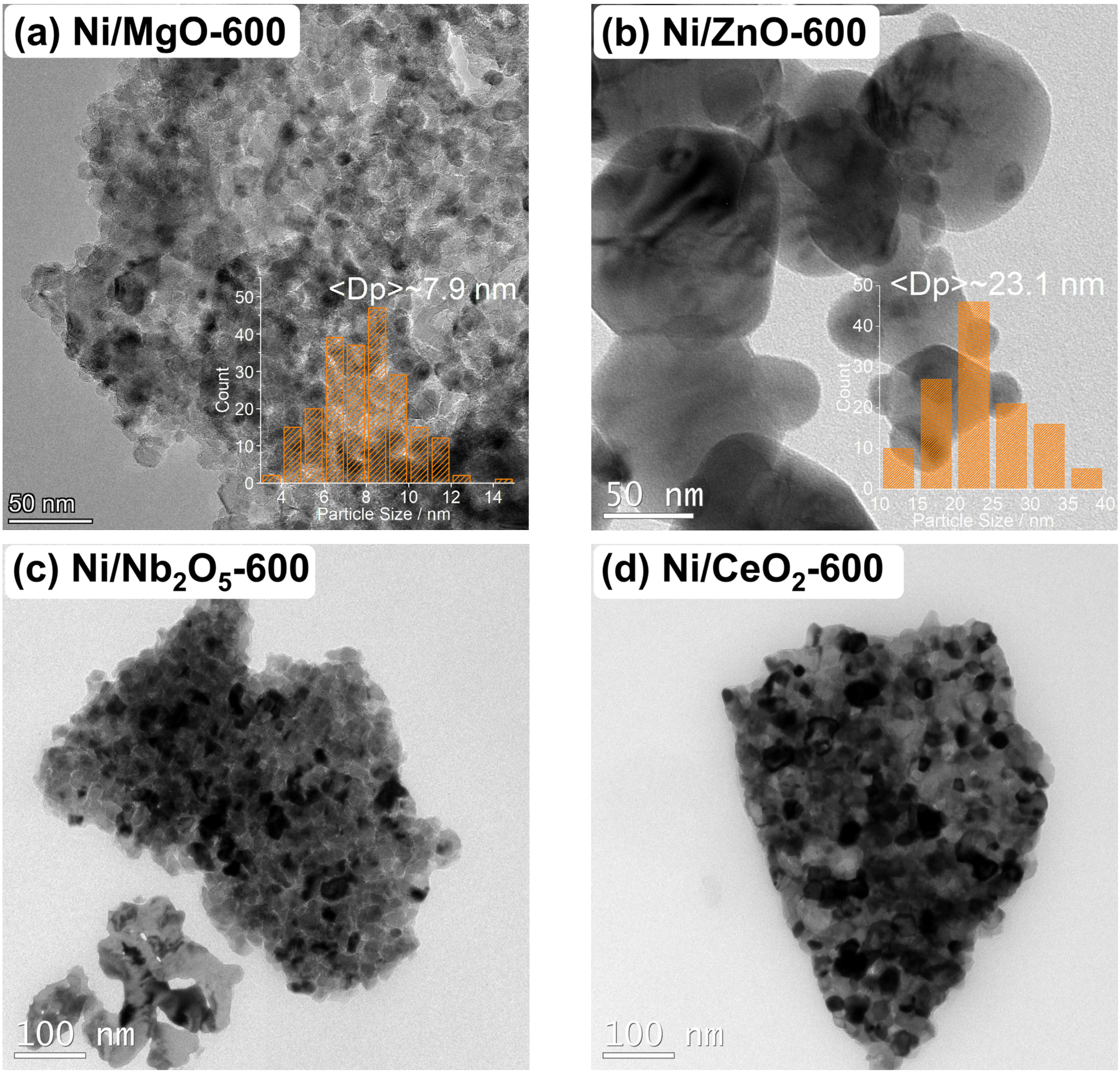


Figure S7. TEM image and Ni particle size distribution of (a) Ni/MgO-600, (b) Ni/ZnO-600, (c) Ni/Nb_2O_5-600, (d) Ni/CeO_2-600.

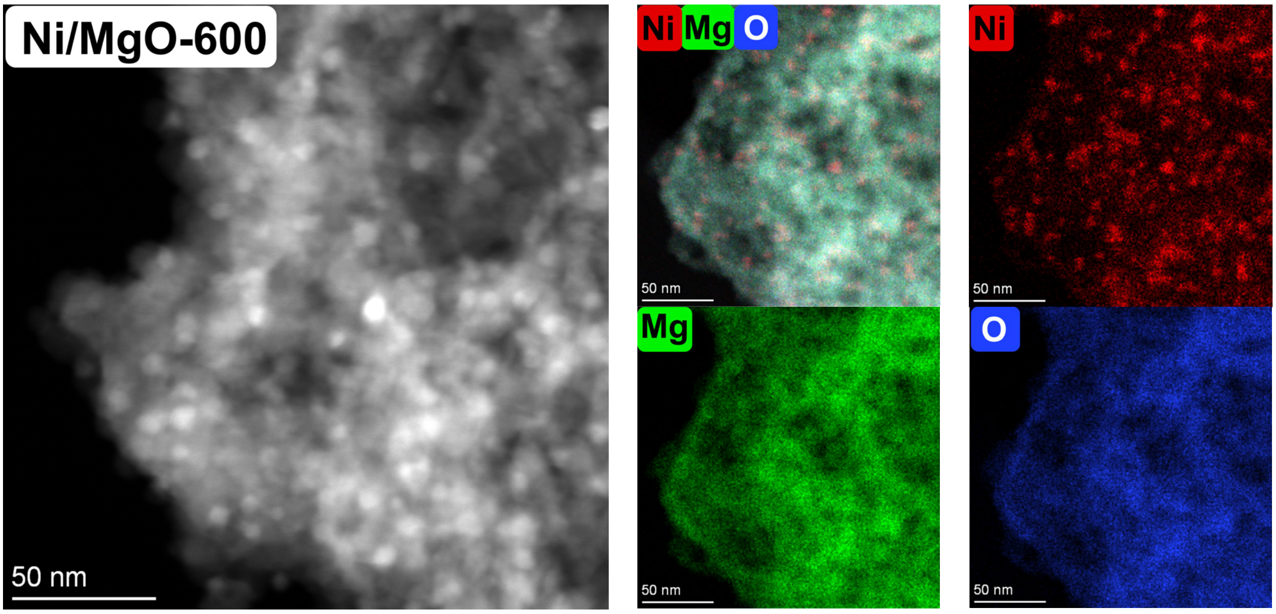


Figure S8. HAADF-STEM image and representative EDS elemental maps of nickel (red), magnesium (green), and oxygen (blue) for Ni/MgO-600.

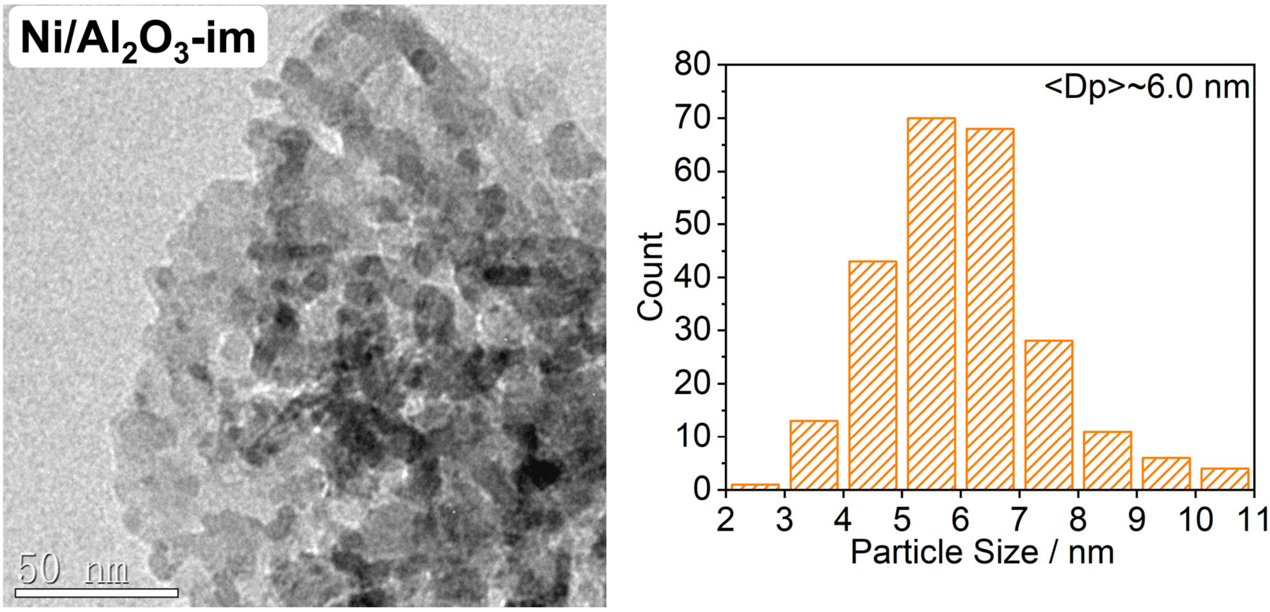
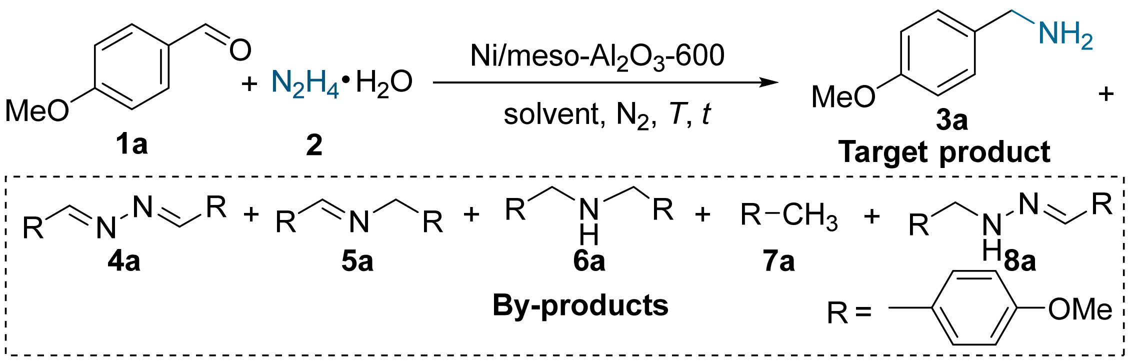


Figure S9. TEM image and Ni particle size distribution of Ni/Al_2O_3-im.

Table S3. Ni/*meso*-Al_2O_3-600 catalyzed reduction of 4-methoxy benzaldehyde (**1a**) and $N_2H_4{\cdot}H_2O$ (**2**) under different reaction conditions [a]



Entry	Solvent	Ni mol%[b]	N_2 (bar)	N_2H_4 (mmol)	solvent volume (mL)	*T* (°C)	Conv. (%)[c]	Yield (%)[c]						
								3a	**4a**	**5a**	**6a**	**7a**	**8a**	**oth-ers**
1	*t*-BuOH	2.5	5	30	5	100	100	**92**	0	3	0	5	0	0
2	MeOH	2.5	5	30	5	100	100	**69**	4	0	16	7	4	0
3	THF	2.5	5	30	5	100	100	**65**	19	2	0	2	0	12
4	toluene	2.5	5	30	5	100	100	**51**	13	24	2	5	0	5
5	*n*-hexane	2.5	5	30	5	100	100	**47**	4	0	44	5	0	0
6	*t*-BuOH	2.5	5	30	3	100	100	**87**	2	4	2	5	0	0
7	*t*-BuOH	2.5	5	30	4	100	100	**86**	9	0	0	3	0	2
8	*t*-BuOH	2.5	5	30	6	100	100	**78**	17	0	0	2	0	3
9	*t*-BuOH	2.5	5	30	7	100	100	**75**	20	0	0	3	0	2
10	*t*-BuOH	2.5	5	10	5	100	100	**12**	15	0	47	7	14	5
11	*t*-BuOH	2.5	5	20	5	100	100	**57**	6	0	30	4	3	0
12	*t*-BuOH	2.5	5	25	5	100	100	**75**	17	0	4	2	0	2
13	*t*-BuOH	2.5	5	35	5	100	100	**91**	2	0	4	4	0	0
14	*t*-BuOH	2.5	5	40	5	100	100	**91**	5	0	4	4	0	0
15	*t*-BuOH	2.5	5	30	5	90	100	**77**	13	4	2	0	4	0
16	*t*-BuOH	2.5	5	30	5	110	100	**81**	1	2	2	13	1	0
17	*t*-BuOH	1.2	5	30	5	100	100	**81**	15	0	0	2	0	2
18	*t*-BuOH	5	5	30	5	100	100	**81**	0	3	0	11	0	5
19	*t*-BuOH	5	1	30	5	100	100	**86**	8	0	1	3	0	2
20	*t*-BuOH	5	10	30	5	100	100	**74**	6	5	0	6	0	6

[a] Reaction conditions: 4-methoxy benzaldehyde (5.0 mmol), hydrazine hydrate, Ni/*meso*-Al_2O_3-600, N_2, 12 h. [b] Based on **1a**. [c] Conversions and yields were determined by GC-MS and GC analysis based on the consumption of **1a**.

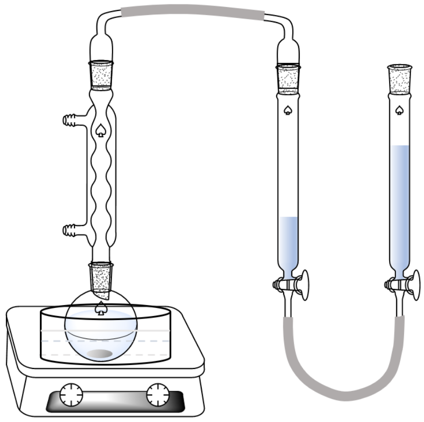
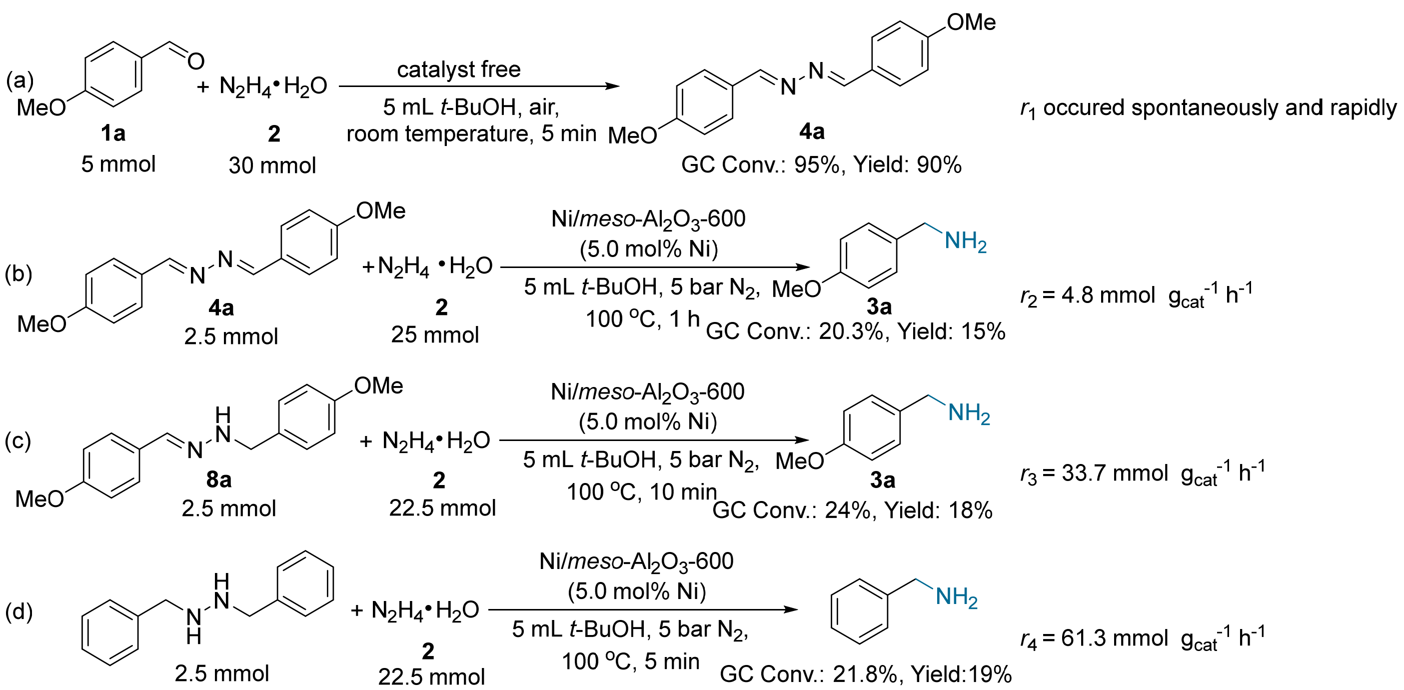


Figure S10. The equipment for hydrazine decomposition reaction. The reaction was initiated by adding 30 mmol hydrazine hydrate into a round bottom flask containing *t*-BuOH (5 mL) and Ni/*meso*-Al_2O_3-600 (106.7 mg). The reaction temperature (100 °C) was controlled by oil bath. The volume change of H_2 and N_2 was detected by a gas barrette and used for the calculation of N_2H_4 conversion. After 12 hrs reaction, 1180 mL gas was produced (calculated at room temperature, ~25 °C). The conversion of hydrazine was calculated by assuming the all the consumed N_2H_4 was converted into H_2 and N_2:

$$Conv.\% = \left[\frac{pV}{R(t/^{o}C + 273.15)} \times \frac{1}{3}\right] / n_{N_2H_4}$$



Scheme S2. Initial reaction rate for steps involved in the N_2H_4-involved reductive amination.

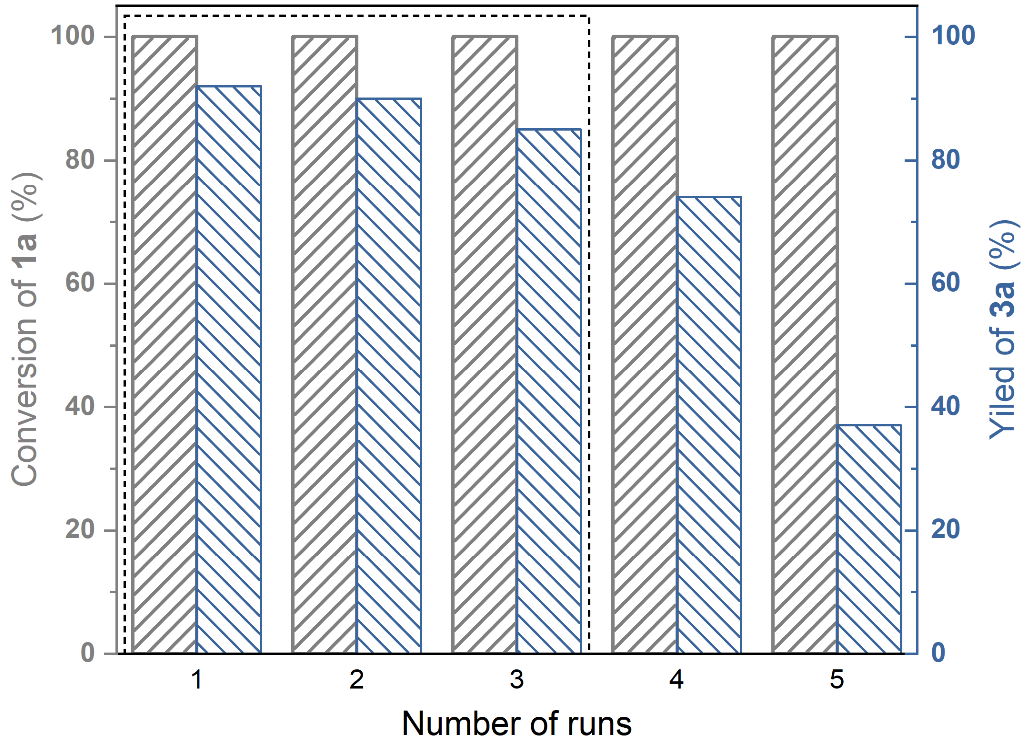
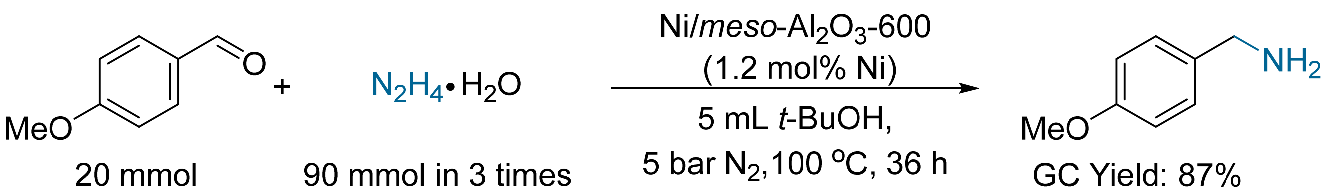


Figure S11. Recycle experiments using Ni/*meso*-Al_2O_3-600 catalyst in the reaction of 4-methoxy benzaldehyde with hydrazine hydrate.



Scheme S3. Gram-scale reductive amination of 4-methoxybenzyl aldehyde with $N_2H_4 \cdot H_2O$.