

Supplementary Materials

Impacts of Ni-Loading Method on the Structure and the Catalytic Activity of NiO/SiO₂-Al₂O₃ for Ethylene Oligomerization

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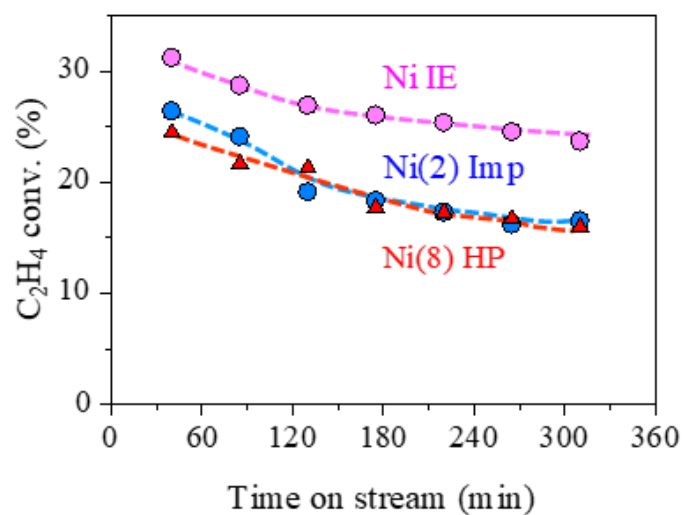


Figure S1. Time course of C_2H_4 conversion over representative Ni/ASA catalysts prepared by an ion-exchange (Ni IE), impregnation (Ni(2) Imp), or one-step homogeneous precipitation (Ni(8) HP) method of Ni loading. Conditions: Catalyst: 0.2 g, temperature: 300 °C, pressure: 0.1 MPa, C_2H_4 : 20 mL/min, N_2 : 20 mL/min.

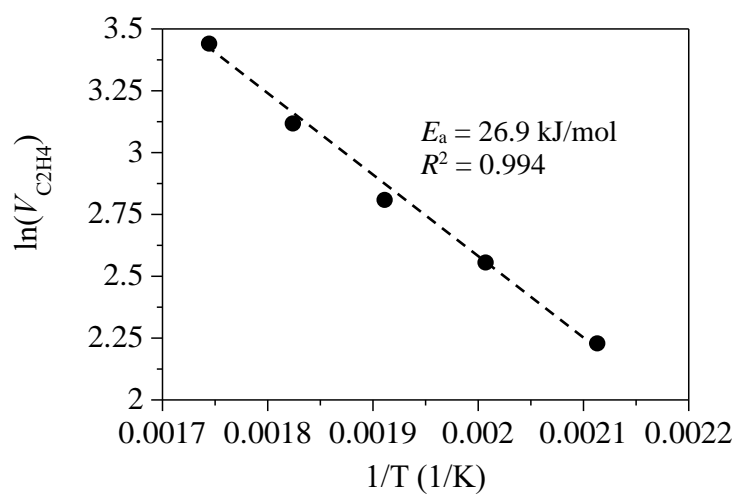


Figure S2. Arrhenius plots for conversion of C_2H_4 over Ni/ASA catalyst prepared by an ion-exchange method of Ni loading (Ni(1.1) IE). Conditions: Catalyst: 0.2 g, temperature: 200–300 °C, pressure: 0.1 MPa, C_2H_4 : 20 mL/min, N_2 : 20 mL/min.

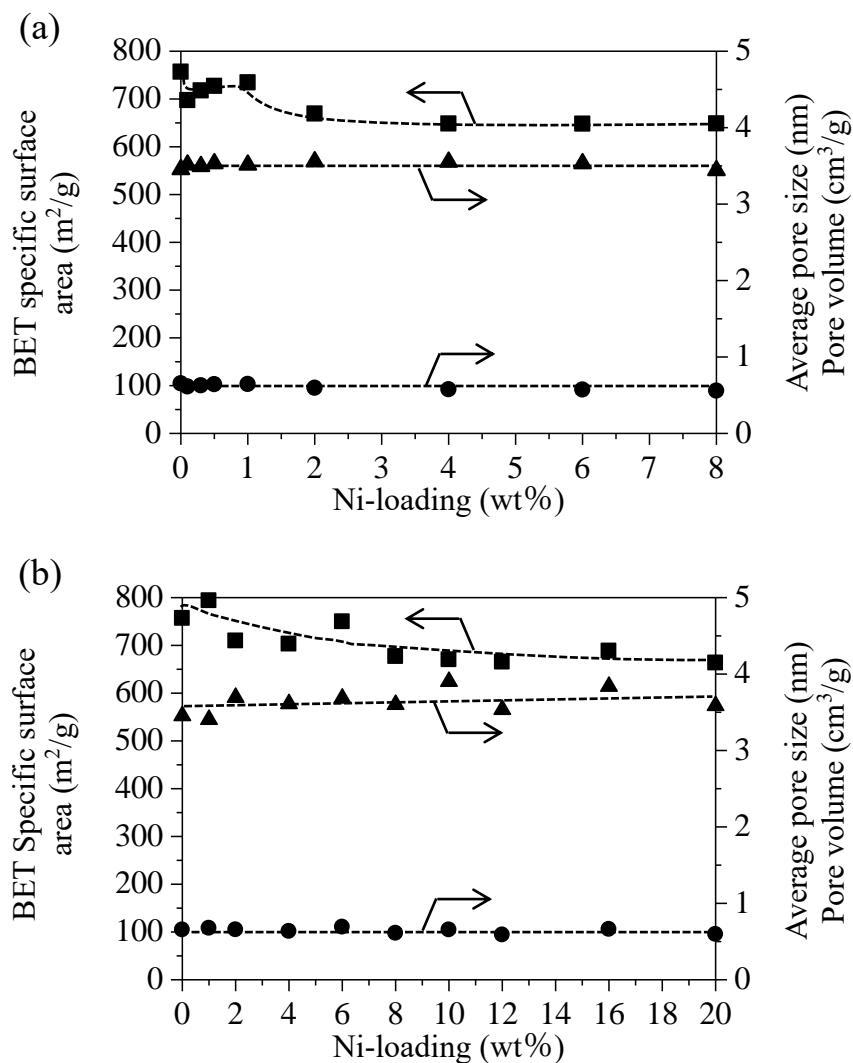


Figure S3. BET specific surface area (black squares), average pore size (black triangles), and pore volume (black circles) of Ni/ASA catalysts prepared by an (a) impregnation or (b) one-step homogeneous precipitation method of Ni loading.

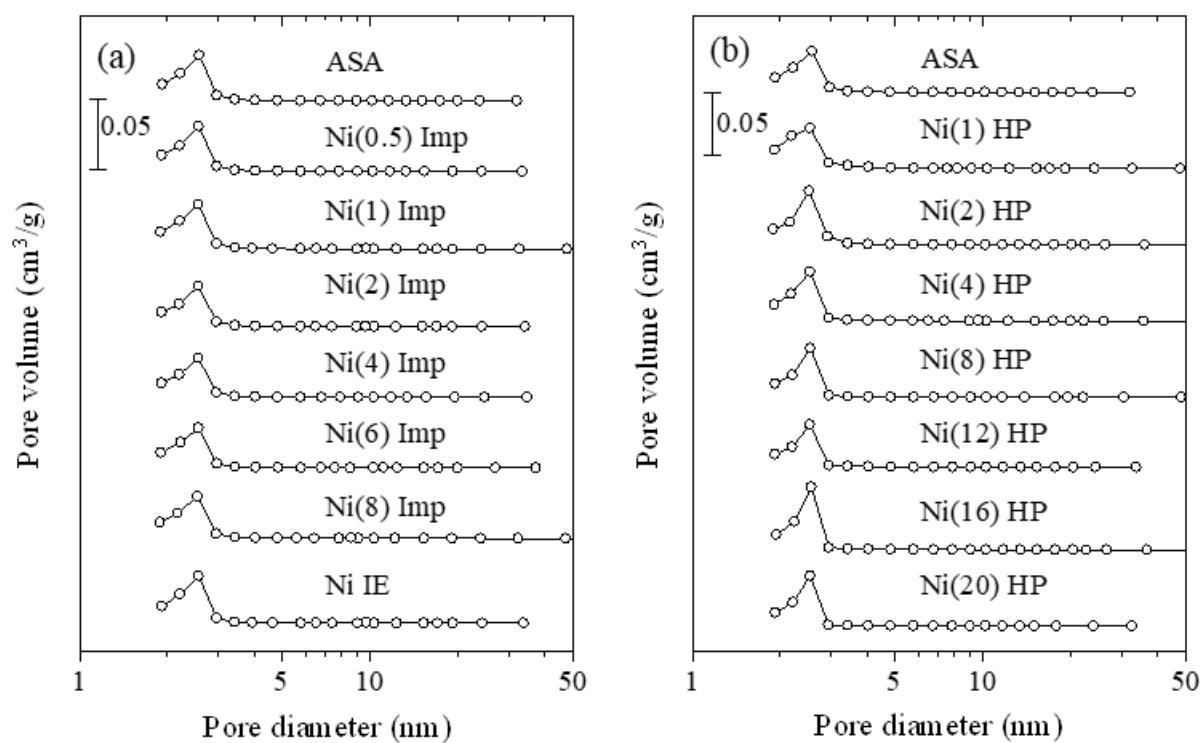


Figure S4. Pore size distribution of Ni/ASA catalysts prepared by an (a) impregnation (Imp) or ion-exchange (IE), or (b) one-step homogeneous precipitation (HP) method of Ni loading.

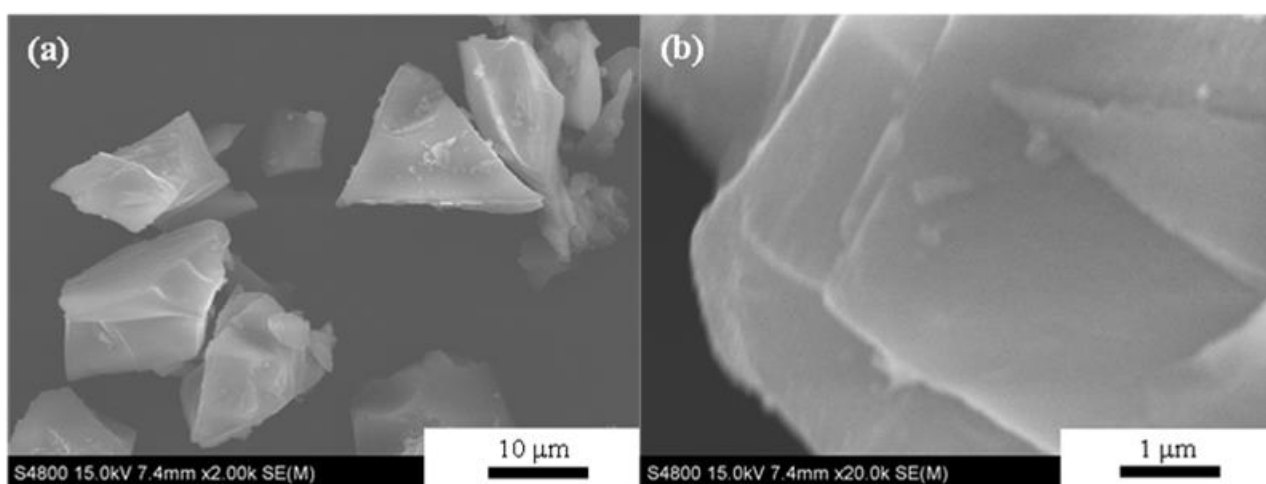


Figure S5. FE-SEM images of Ni/ASA catalyst prepared by an ion-exchange method of Ni loading (Ni(1.1) IE).

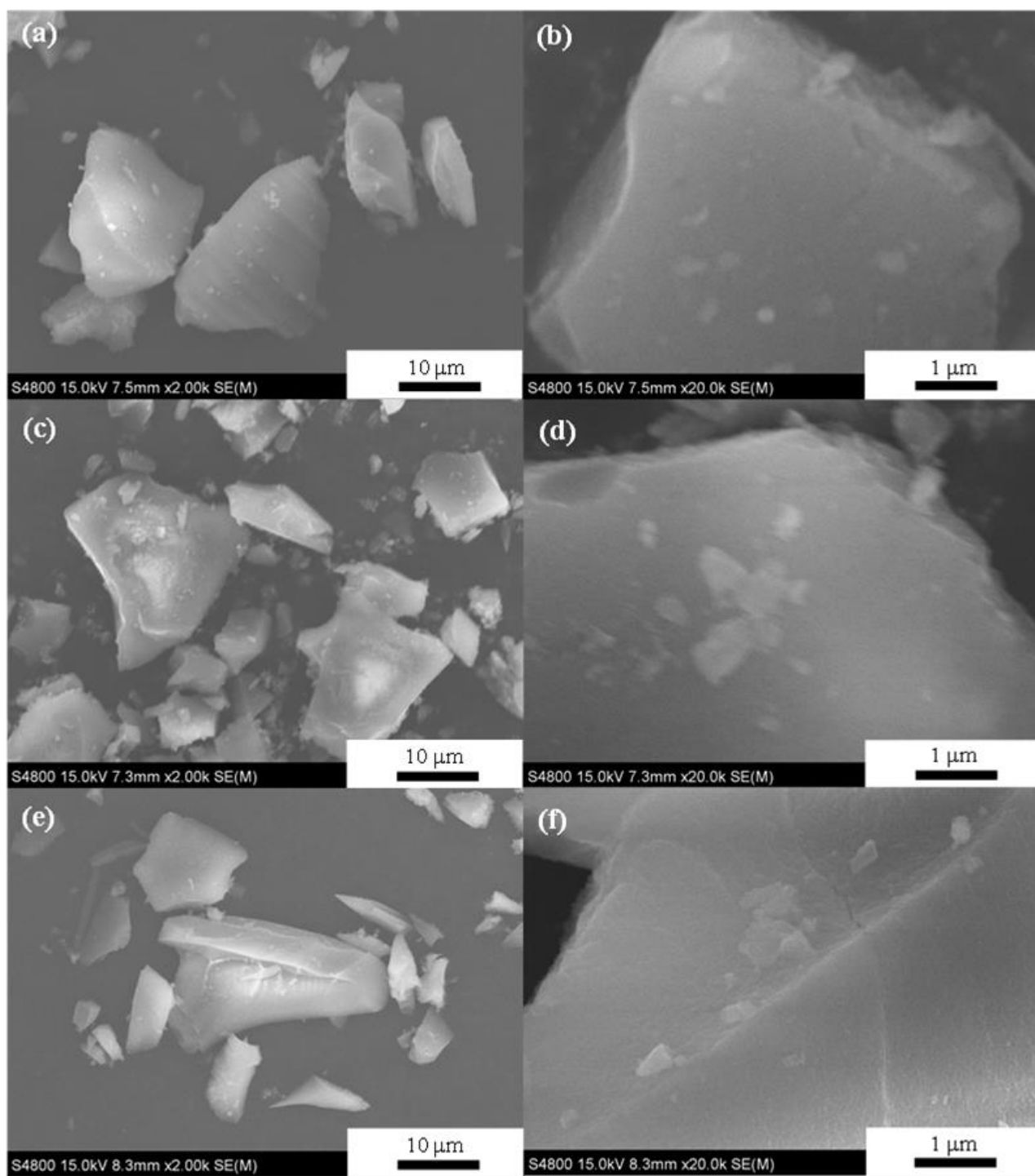


Figure S6. FE-SEM images of representative Ni/ASA catalysts prepared by a one-step homogeneous precipitation (HP) method of Ni loading: (a, b) Ni(1) HP, (c, d) Ni(8) HP, (e, f) Ni(16) HP.

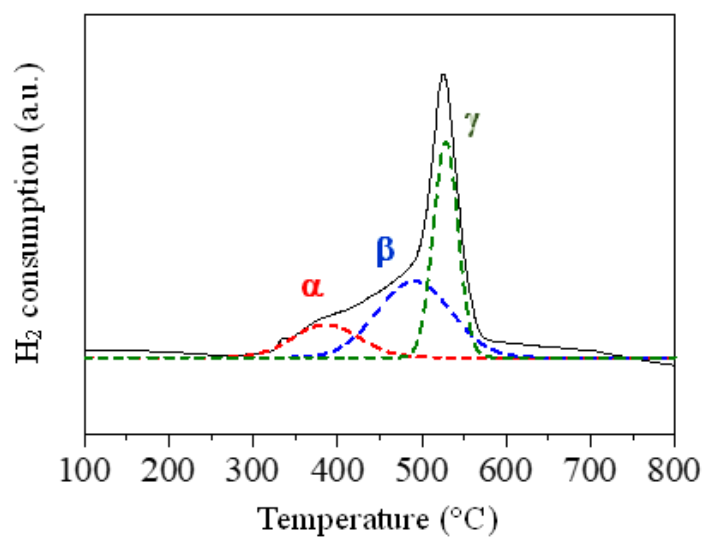


Figure S7. Peak deconvolution of the H₂-TPR profile of a representative Ni/ASA catalyst prepared by an impregnation method of Ni loading: Ni(2) Imp. Solid and dotted lines represent the observed and deconvoluted profiles, respectively. α : peak attributed to bulk-like NiO particles; β : peak attributed to small NiO particles; γ : peak attributed to ion-exchanged Ni cations.

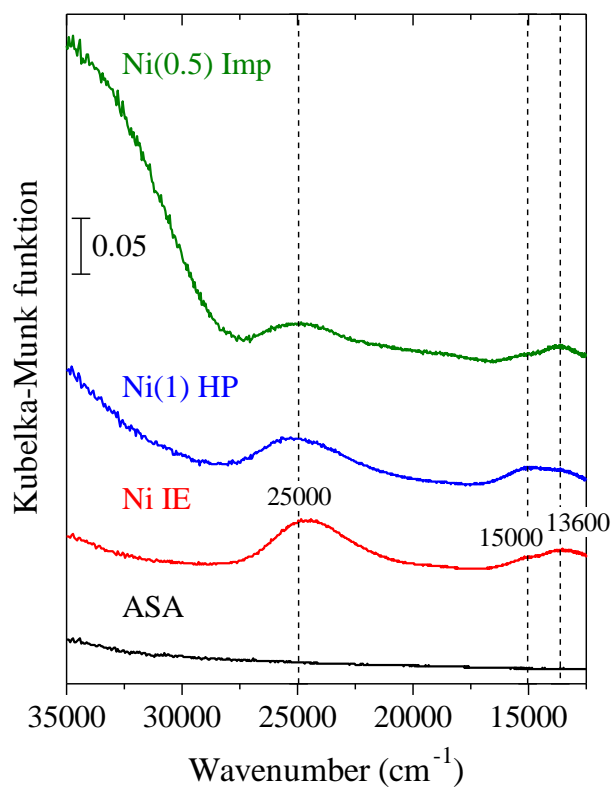
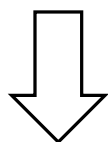
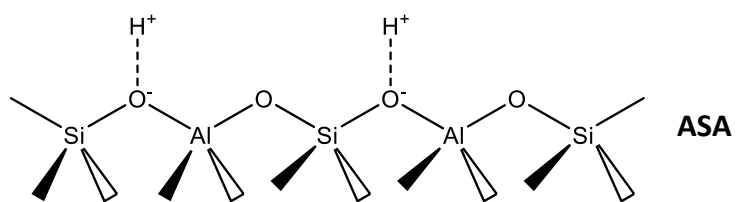
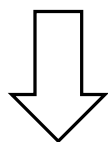
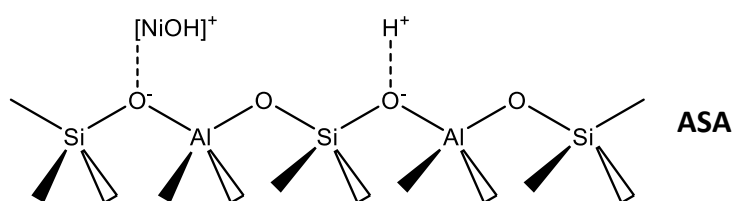


Figure S8. Diffuse reflectance UV-vis spectra of the ASA support and Ni/ASA catalysts prepared by an ion-exchange (Ni IE), impregnation (Ni(0.5) Imp), or one-step homogeneous precipitation (Ni(1) HP) method of Ni loading.



Ion-exchange with Ni(NO₃)₂
aqueous solution



Calcination at 450 °C

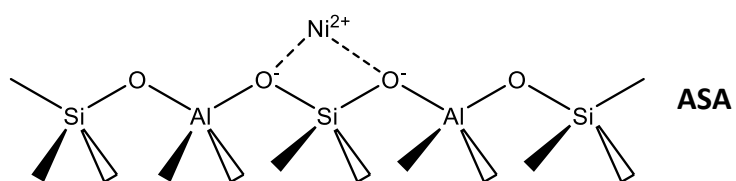


Figure S9. Proposed structure of ion-exchanged Ni cation in Ni/ASA catalyst.

Table S1. Comparison of catalytic activity of Ni-containing heterogeneous catalysts in EO

Catalyst	Ni (wt%)	Ni-loading method	Temperature (°C)	Pressure (MPa)	Activity ^a (g/g/h)	Activity at 0.1 MPa ^b (g/g/h)	Ref.
Ni-Y	5.6	Impregnation	60	2.8	0.3	0.1	10
Ni-Beta	2.5	Ion-exchange	120	2.6	1.6	0.4	11
Ni/Beta	5.2	Impregnation	120	0.1	0.2	0.2	48
Ni/Al-MCM-41	5.7	Impregnation	120	0.1	0.9	0.9	48
Ni-Al-SBA-15	2.6	Ion-exchange	150	3.0	9.1	2.3	34
Ni-AlSiO ₂	2.0	Ion-exchange	150	3.0	9.0	2.3	35
Ni-SiO ₂ -Al ₂ O ₃	1.6	Ion-exchange	110	3.5	1.9	0.5	58
Ni-SiO ₂ -Al ₂ O ₃	0.27	Ion-exchange	300	1.2	3.7	1.4	19
NiO/SiO ₂ -Al ₂ O ₃	4.0	Impregnation	300	0.1	1.6	1.6	53
NiO/SiO ₂ -Al ₂ O ₃	4.0	Impregnation	300	0.1	1.8	1.8	54
Ni IE	1.1	Ion-exchange	300	0.1	2.3	2.3	This work

^a Data from references [1] and [57]. Complete units: (g of oligomers)/(g of catalyst)/h.

^b Activity at 0.1 MPa was calculated assuming that the reaction rate for EO was 0.4th order with respect to pressure. Complete units: (g of oligomers)/(g of catalyst)/h.

Table S2. Activation energies of representative Ni/ASA catalysts

Catalyst	Activation energy
	(kJ/mol)
Ni IE	26.9
Ni(1) Imp	29.3
Ni(8) Imp	21.2
Ni(8) HP	24.5
Ni(12) HP	20.9

Table S3 Crystallite size of NiO and NiSiO₃, as measured by XRD

Catalyst	Crystallite size (nm)	
	NiO	NiSiO ₃
Ni(1) Imp	n.d.	n.d.
Ni(2) Imp	11.4	n.d.
Ni(4) Imp	11.6	n.d.
Ni(6) Imp	9.2	n.d.
Ni(8) Imp	9.9	n.d.
Ni(1.1) IE	n.d.	n.d.
Ni(1) HP	n.d.	n.d.
Ni(2) HP	n.d.	n.d.
Ni(4) HP	n.d.	7.8
Ni(8) HP	n.d.	8.0
Ni(12) HP	n.d.	5.3
Ni(16) HP	n.d.	5.7
Ni(20) HP	n.d.	5.5

n.d.: not detected. Crystallite sizes of NiO and NiSiO₃ were calculated from the diffraction lines at 43.2 and 60.7 degrees, respectively, using the Scherrer equation.

Table S4. Deconvolution of H₂-TPR profiles of Ni/ASA catalysts prepared by an impregnation method

Catalyst	Ratio (%)			Amount (wt%)		
	Large NiO	Small NiO	Ion-exchanged	Large NiO	Small NiO	Ion-exchanged
	particles	particles	Ni cations	particles	particles	Ni cations
Ni(1) Imp	6.0	41.0	53.0	0.06	0.41	0.53
Ni(2) Imp	20.1	38.7	41.2	0.40	0.78	0.82
Ni(4) Imp	39.0	40.1	20.9	1.56	1.60	0.84
Ni(6) Imp	23.0	52.4	24.6	1.38	3.14	1.48
Ni(8) Imp	60.3	26.2	13.5	4.82	2.10	1.08

Table S5. Amounts of acidic sites in ASA and Ni/ASA, as calculated from NH₃-TPD profiles

Entry	Catalyst	Amount of acidic sites (mmol/g)			Total
		Weak	Medium-strength	Strong	
		(<400 °C)	(400–600 °C)	(>600 °C)	
1	ASA	0.49	0.14	0.50	1.13
2	Ni(1.1) IE	0.62	0.35	0.54	1.51
3	Ni(1) Imp	0.61	0.41	0.52	1.54
4	Ni(2) Imp	0.67	0.49	0.49	1.65
5	Ni(4) Imp	0.63	0.42	0.50	1.55
6	Ni(6) Imp	0.63	0.42	0.50	1.55
7	Ni(8) Imp	0.62	0.36	0.46	1.44
8	Ni(1) HP	0.50	0.22	0.56	1.28
9	Ni(2) HP	0.49	0.23	0.56	1.28
10	Ni(4) HP	0.51	0.26	0.67	1.44
11	Ni(8) HP	0.56	0.28	0.69	1.53
12	Ni(12) HP	0.61	0.32	0.85	1.78
13	Ni(16) HP	0.70	0.35	0.88	1.93
14	Ni(20) HP	0.71	0.40	1.08	2.19
15	NiSiO ₃	0.47	0.55	1.33	2.35