Supporting information for

Nitrate Reduction on the Surface of Bimetallic Catalysts Supported by Nano-crystalline Beta-zeolite (NBeta)

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Characterization of catalysts

The procedures of sample preparation and analyses for characterization were followed from our previous studies.[1-4] However, a brief description of the procedures is given below.

XRD analysis of powder NBeta, Sn-Pd-NBeta, Cu-Pd-NBeta and In-Pd-NBeta catalysts was conducted by Rigaku automated diffractometer with Cu-KN radiation (D/MAX-2500, Rigaku, Japan). The scan range was 2º to 80º 2θ and scan speed was 2º min^{-1}.

The FT-IR spectra of NBeta, Sn-Pd-NBeta, Cu-Pd-NBeta and In-Pd-NBeta samples were obtained by Nicolet 740 FT-IR spectrometer at ambient conditions and using KBr as the diluent.

Morphology of NBeta and dispersion of Sn, Cu, In and Pd on NBeta surface was analyzed by SEM/EDX (Magellan400, FEI). Samples were prepared by carefully packing of powder catalysts to carbon tape on an SEM template. Osmium coating was applied prior to analysis and the samples were analyzed by SEM at 10 kV.

The morphology of NBeta, Sn-Pd-NBeta, Cu-Pd-NBeta and In-Pd-NBeta catalysts was also characterized by TEM (JEM-3010 model, JEOL). Few milligrams of powder catalysts were dissolved in ethanol and sonicated for 10 min to disperse particles. Samples were prepared by adding several drops of ethanol solution of catalysts on 300-mesh gold TEM grid with a carbon film. The samples were dried in anaerobic chamber for 1 h and then analyzed by TEM at 300 kV.

Surface area of NBeta was measured by nitrogen adsorption and desorption at −196 ◦C with BET surface analyzer (ASAP 2010, Micrometrics).

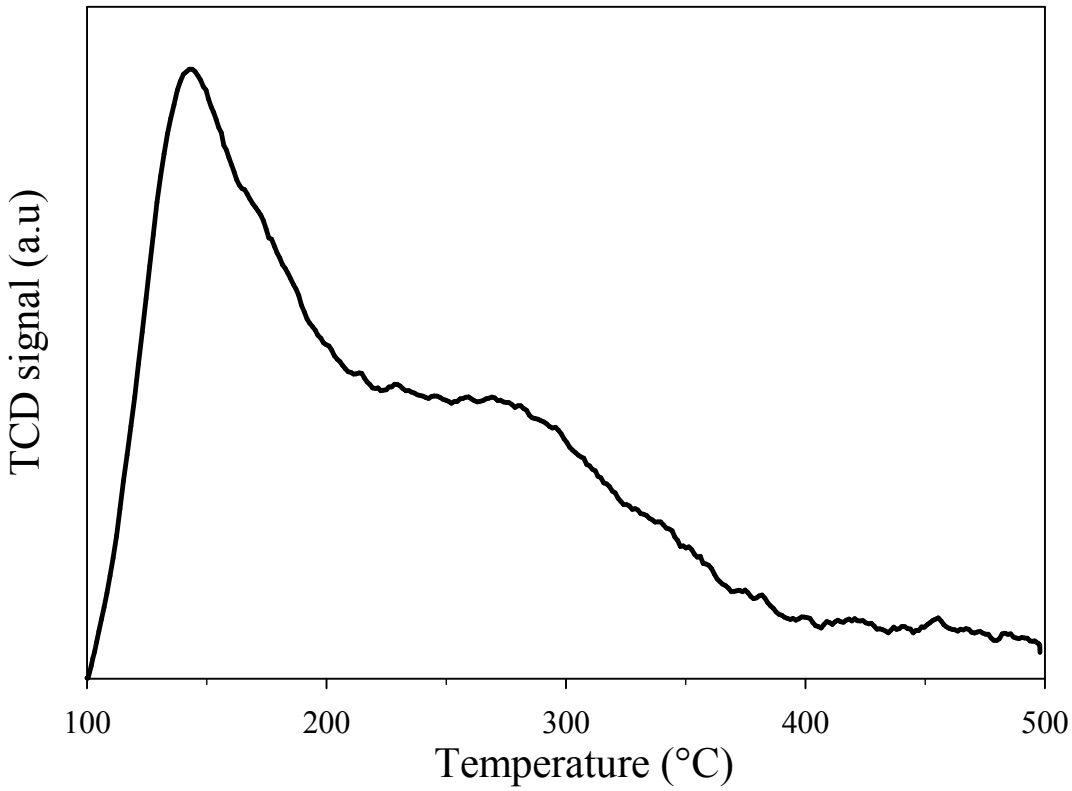
Leaching of Sn, Cu, In and Pd were estimated by ICP-MS. The sample was immediately filtered using a 0.2 μm membrane filter.

The oxidation states of Sn, Cu, In and Pd were identified by XPS analysis (Sigma Probe, Thermo Scientific, USA) on the surface of NBeta for three conditions i.e. 1) as prepared

catalysts, 2) after reduction with $NaBH_4$ and 3) after NO_3^- reduction reaction. All the catalysts were collected using a 0.2 μm membrane filter in a vacuum filtration assembly, and dried under freeze-vacuum condition. The dried samples were carefully shifted to XPS templates inside of anaerobic chamber to avoid surface oxidation via ambient oxygen. The C 1s peak at 284.8 eV was used as a reference for adjusting the surface charging effects.

Zeta-potential of Sn-Pd-NBeta, Cu-Pd-NBeta and In-Pd-NBeta suspensions was measured in pH range 3-8.5. Buffer solutions for different pH adjustment were prepared as following: 0.1 M acetate buffer solution was prepared by mixing acetic acid and sodium acetate, 0.1 M phosphate solutions were prepared by mixing a) potassium phosphate and sodium phosphate dibasic heptahydrate and b) sodium phosphate dibasic and hydrochloric acid. The catalysts were reduced by $NaBH_4$ and added into the prepared buffer solutions. All the solutions containing catalyst samples were ultra- sonicated for 30 min to disperse the samples before analysis with zetasizer (Zetasizer Nano ZS, Malvern, Korea).

NH_3-TPD was performed by AutoChem II 2920 (micromeritics USA). To remove the impurities, the sample was heated at 10 °C min^{-1} until 550 °C under the constant flow of helium. Then sample ws cooled down to 100 °C and saturated with NH_3 for 90 min. Then the temperature was increased to 500 °C at 10 °C min^{-1}.



SI Fig. S1 Profile of NH3- desorption profile of NBeta conducted temperatured programmed desorption.

Table S1 Surface area and pore size distributions of catalysts

Catalyst	BET-SA (m^2/g)	External-SA (m^2/g)[a]	Pore volume (cc/g)[b]	Pore size (nm)[c]
NBeta	664	241	0.35	3.12
Sn-Pd-NBeta	608	195	0.31	3.05
Cu-Pd-NBeta	597	201	0.32	2.91
In-Pd-NBeta	613	182	0.29	2.86

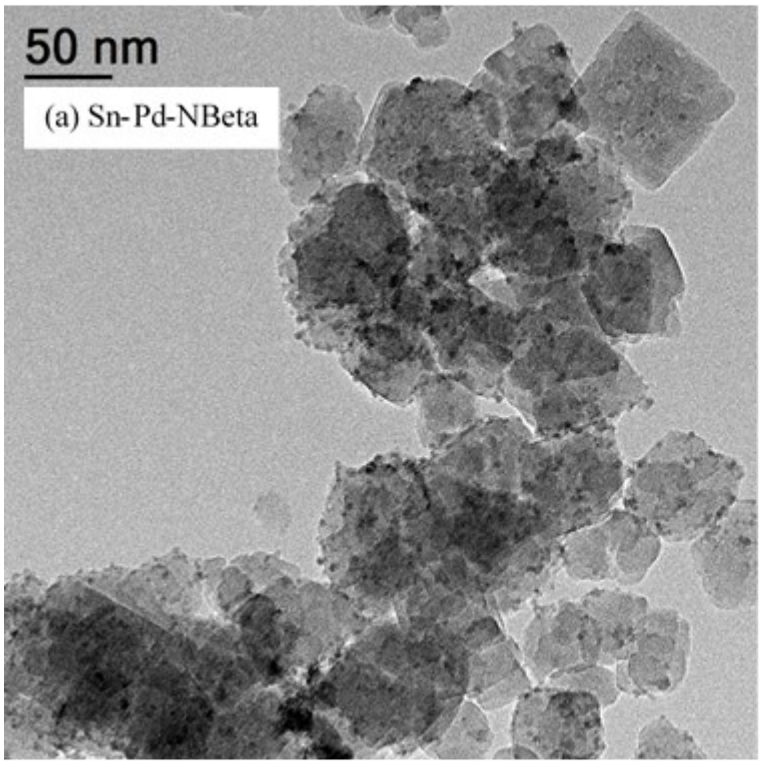
[a] *t*-Plot method.
[b] Pore volume calculated from the desorption branch of N_2 physisorption isotherm.
[c] BJH desorption average pore diameter.

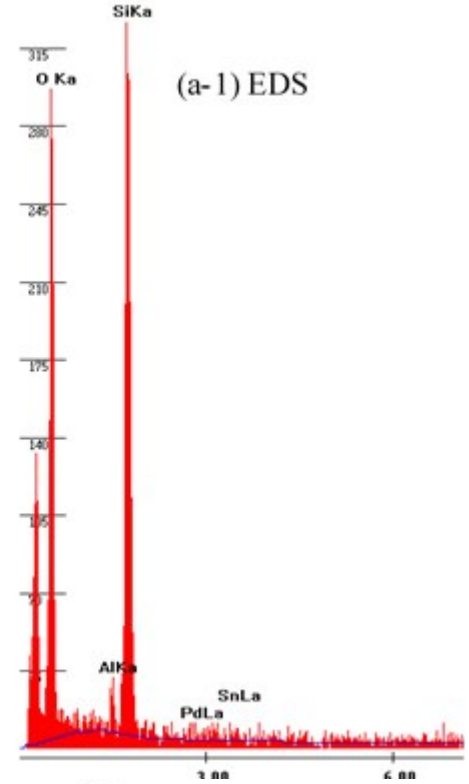
Table S2 Comparison of performance of bimetallic catalysts for NO_3^- reduction at different experimental conditions.

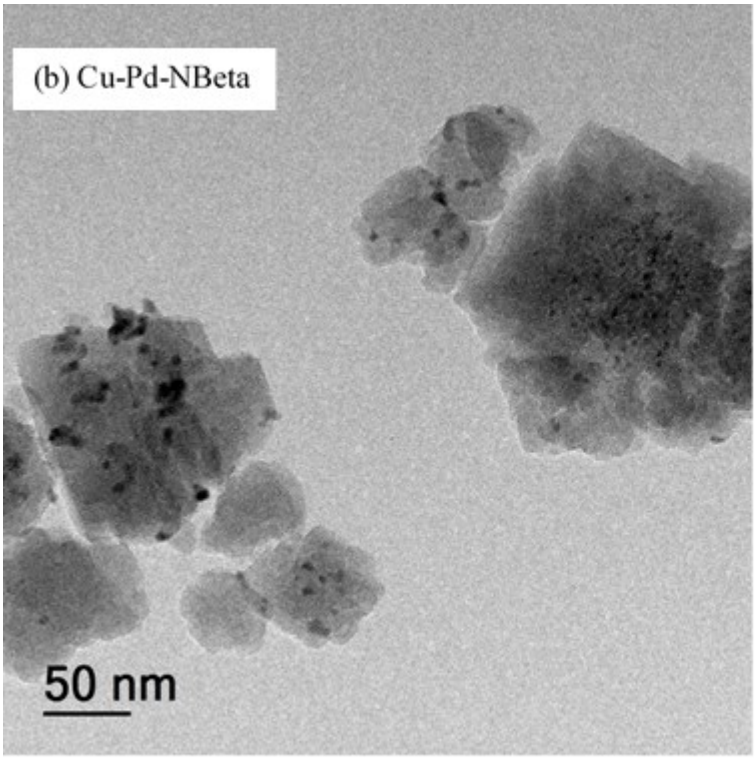
Initial NO_3^- concentration (mg/L)	The amount of catalyst (g/L)	Support (Pd-M)	BET surface area of support material (m^2/g)	Reducing agent	Buffer	k ($10^{-2}\times min^{-1}$)	K' ($10^{-2}\times min^{-1}g_{cat}^{-1}$)	K" ($10^{-2}\times L.min^{-1}g_{Pd}^{-1}$)	NO_3^- Removal (%)	N_2 Selectivity (%)	NH_4^+ Selectivity (%)	Ref.
221.43	1	TiO_2 3%Pd:1%Cu	50	H_2(100mL/min)	Mes buffer	4.80 **	23.98 **	159.6 **	100	50.2	49.7	1
132.8	1.25	α-Fe_2O_3 2.8%Pd:1.6%Cu	12.7	H_2(30mL/min)	CO_2(40mL/min)	3.27 **	13.06 **	93.29 **	96.4	70	30	2
132.8	2.5	NZSM5 1.6%Pd:1.6%Sn	447	H_2(30mL/min)	CO_2(60mL/min)	16.40**	65.6**	410**	100	91.13	9.87	4
100	0.8	ASA 5%Pd:1.25%Cu	375	H_2(200mL/min)	CO_2(100mL/min)	6.45 **	16.14 **	161.25***	100	90.2	9.8	5
100	2.22	Al_2O_3 4%Pd:1%Cu	196	H_2(0.15atm)	0.2M HCl	12.97 **	6.49 **	145.91***	100	82.3	17.7	6
100	1	TiO_2 2%Pd:1%Cu	50	H_2(60mL/min)	CO_2	6.66 **	66.62 **	333***	90	76	19	7
100	0.6	Al_2O_3 2%Pd:1.7%Cu	196	H_2(90mL/min)	CO_2(100mL/min)	5.85 **	12.99 **	487.5 ***	100	74	7.6 mg/L	8
100	0.51	ACo 2%Pd:1%Cu	869	H_2(200Ncm^3/min)	CO_2(200Ncm^3/min)	0.88 **	2.21 **	86.9**	99	43	57	9
100	0.51	CNT-TiO_2 1%Pd:1%Cu	131	H_2(200Ncm^3/min)	CO_2(200Ncm^3/min)	1.83 **	4.57 **	361.43 **	100	66	34	10
100	0.51	TiO_2 1%Pd:1%Cu	50	H_2(200Ncm^3/min)	CO_2(200Ncm^3/min)	1.76 **	4.40 **	347.6**	95	17	83	10
100	0.51	Ac-Mn 1%Pd:1%Cu	269	H_2(200Ncm^3/min)	CO_2(200Ncm^3/min)	0.31 **	0.77 **	61.23 **	59	60	40	10
177.14	7.69	Iron 0.3%Pd:0.5%Cu	0.51	-	-	0.67 *	1.34 **	29.03**	91.5	29.6	65.6	11
100	0.51	ACo 2%Pd:1%Cu	869	H_2(200Ncm^3/min)	CO_2(200Ncm^3/min)	0.43 **	1.07 **	42.46**	67	55	44	12
100	1.62	Al_2O_3 5%Pd:1.25%Cu	196	H_2(500mL/min)	pH 6	18.08 **	22.60 **	232.65 **	100	82	5.1 mg/L	13
100	1	AC 2%Pd:0.4%Cu	869	H_2(333mL/min)	CO_2(333mL/min)	3.73 **	3.73 **	186.5**	74.4	51.3	48.3	14
124	1	Al_2O_3 5%Pd:1.25%Sn	196	H_2(50mL/min)	pH 5	3.39 **	3.39 **	67.8**	99	97	3	15
100	0.48	Al_2O_3 4.4%Pd:1.21%Sn	155	H_2(90mL/min)	CO_2(90ml/min)	1.23	3.51	58.31	100	88	12	16
132.8	2.5	NBeta 1.6%Pd:2.2%Cu	664	H_2(30mL/min)	CO_2(60mL/min)	2.31	9.24	57.75	100	92.68	7.32	This study

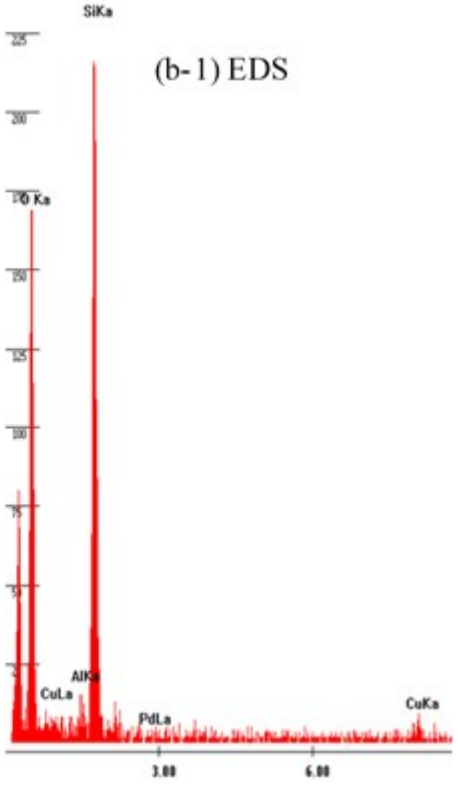
132.8	2.5	NBeta 1.6%Pd:2.2%In	664	H_2(30mL/ min)	CO_2(60m L/min)	2.89	11.56	72.25	100	82.93	17.07	This study
132.8	2.5	NBeta 1.6%Pd:2.2% Sn	664	H_2(30mL/ min)	CO_2(60m L/min)	19.09	76.36	477.25	100	80.80	19.2	This study

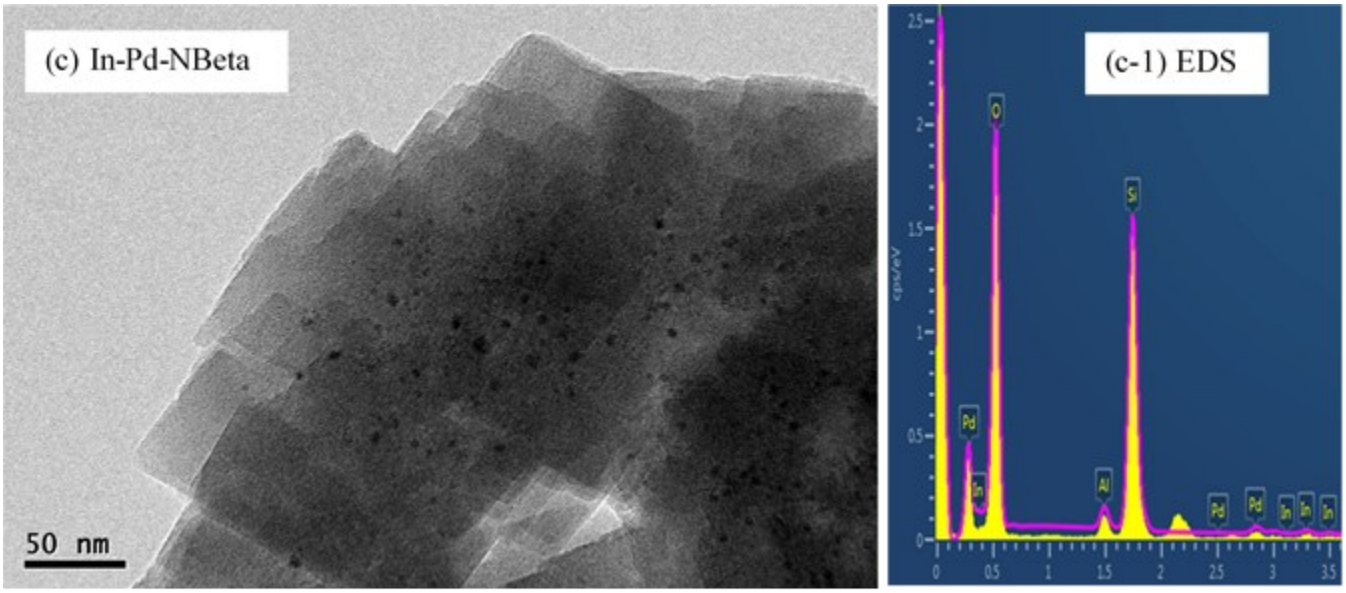
*kinetic rate constant previously published in the literature.
**kinetic rate constants and catalyst loading normalized rate constants calculated from this study using previously published datasets.
***Only those values were selected which have R^2 values >0.95 for the first-order curve fitting using the previously published datasets.


50 nm
(a) Sn-Pd-NBeta

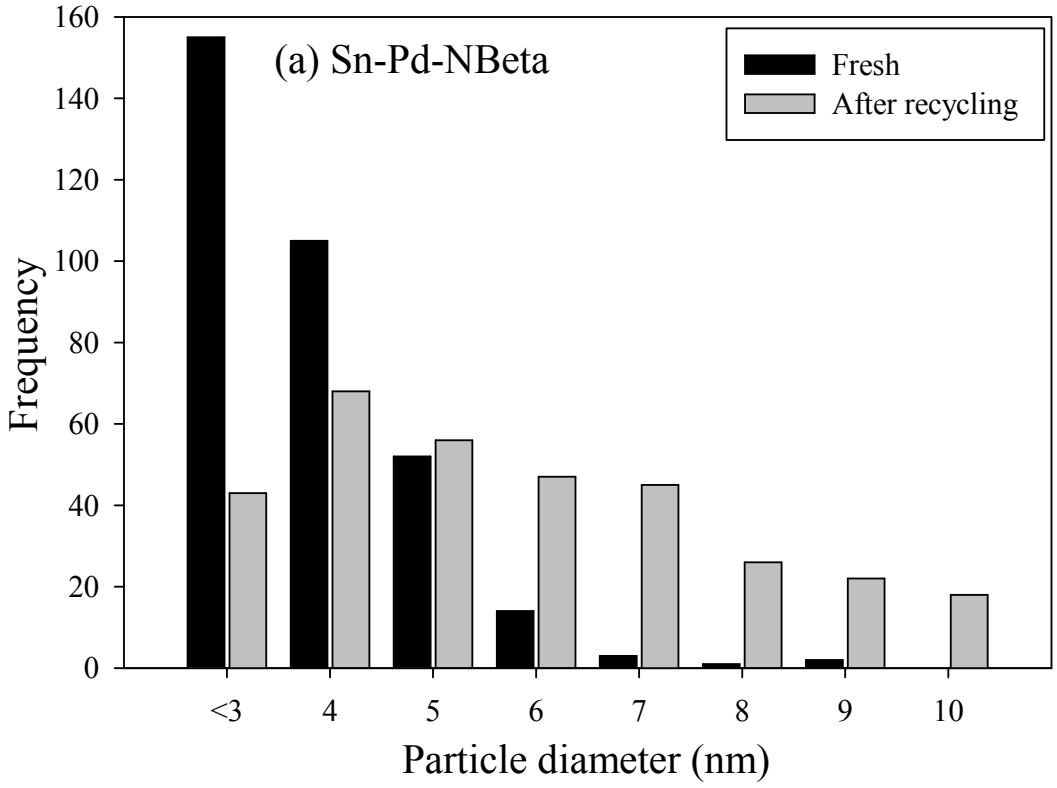

SiKa
O Ka
(a-1) EDS
AlKa
SnLa
PdLa

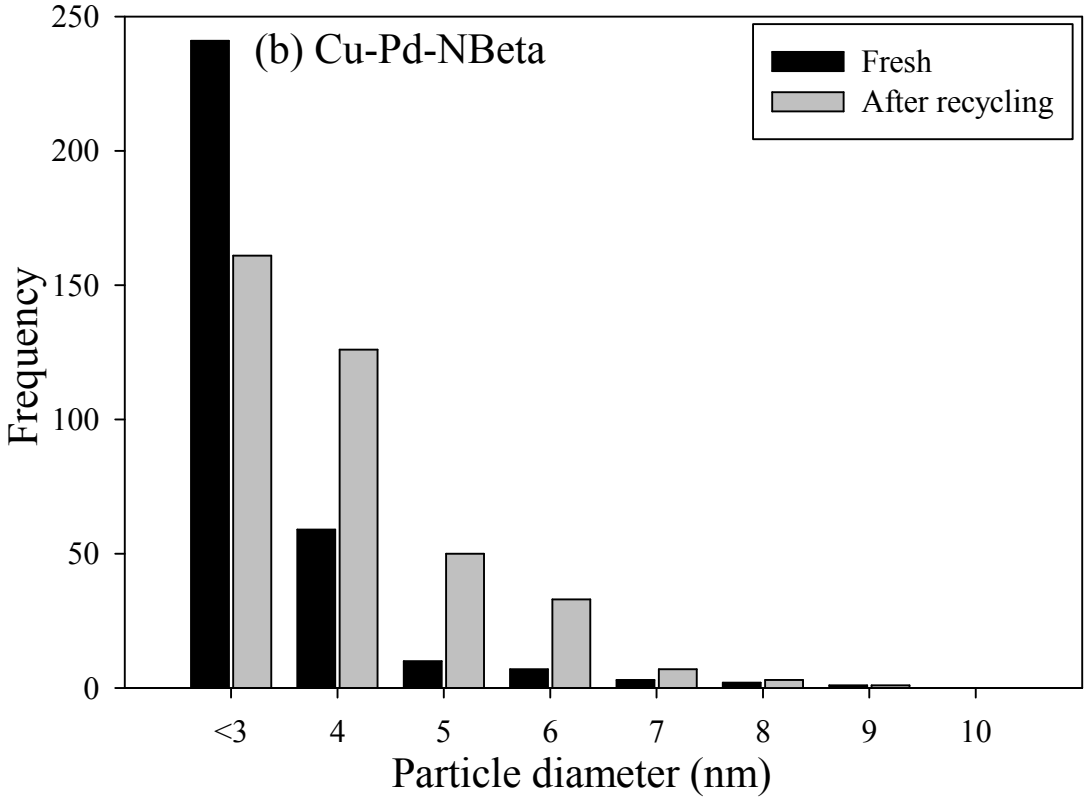

(b) Cu-Pd-NBeta
50 nm

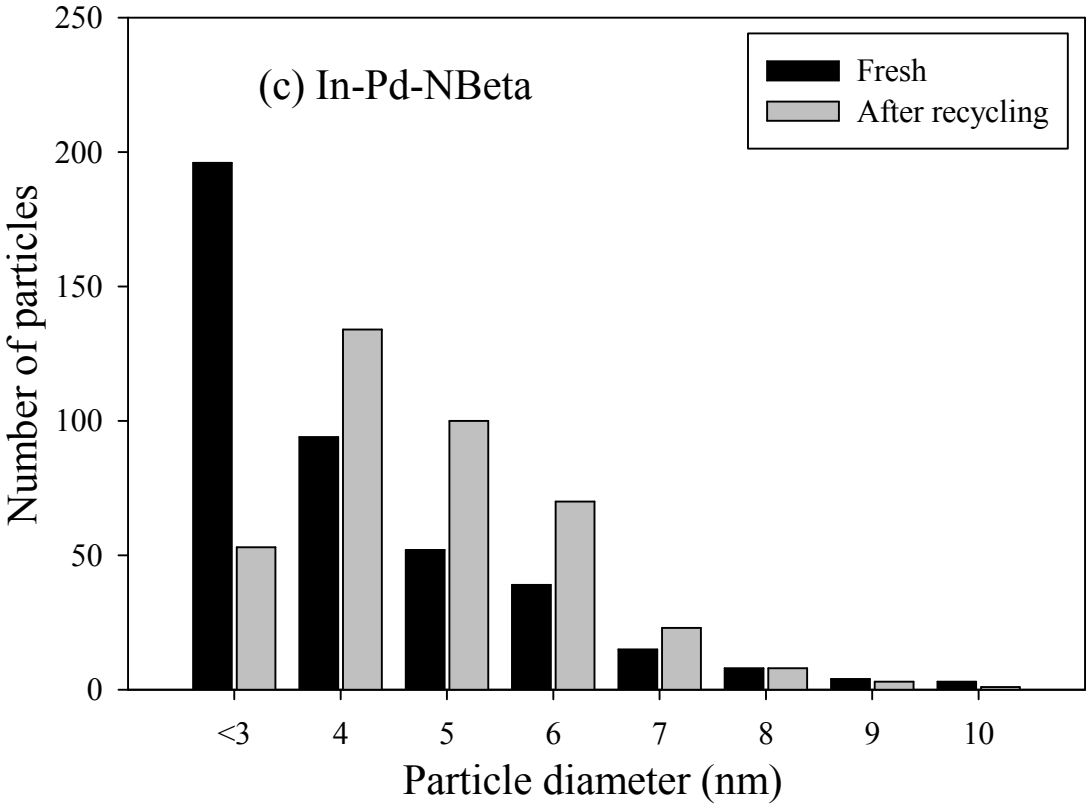

SiKa
O Ka
(b-1) EDS
AlKa
CuLa
PdLa
CuKa



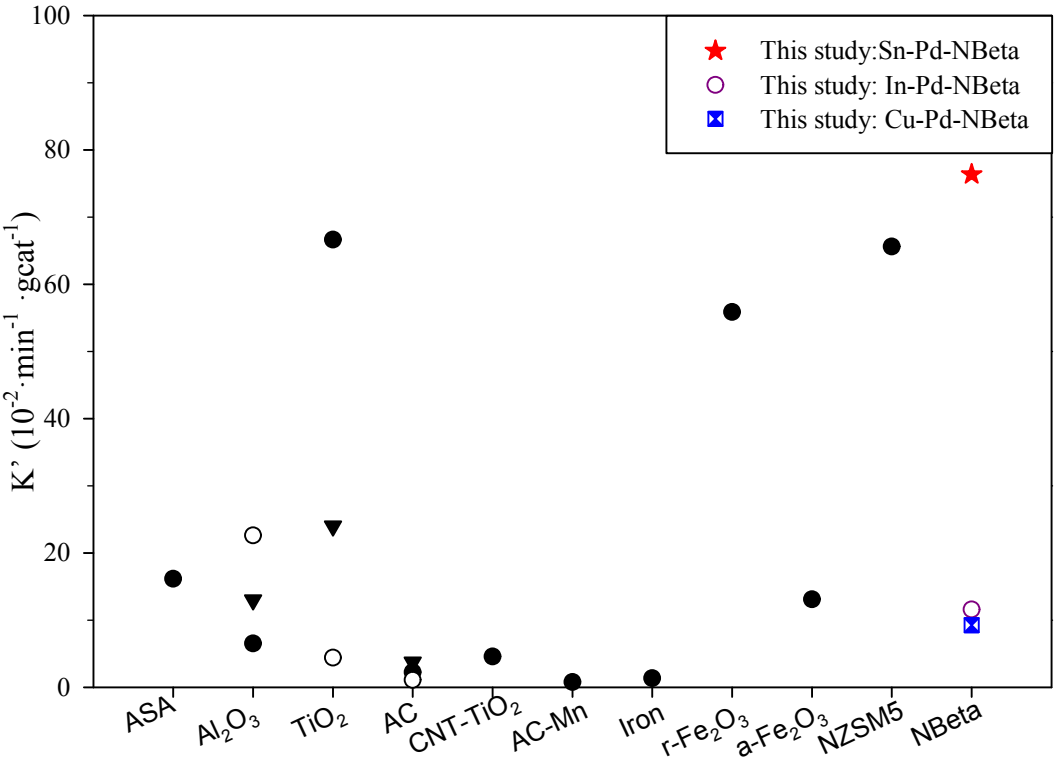
SI Fig. S2 TEM images and EDX spectra of (a) Sn-Pd-NBeta, (b) Cu-Pd-NBeta, and (c) In-Pd-NBeta after recycling.


(a) Sn-Pd-NBeta
Fresh
After recycling
Frequency
160
140
120
100
80
60
40
20
0
<3
4
5
6
7
8
9
10
Particle diameter (nm)


(b) Cu-Pd-NBeta
Fresh
After recycling
Frequency
250
200
150
100
50
0
<3
4
5
6
7
8
9
10
Particle diameter (nm)



SI Fig. S3 Particle size histogram of (a) Sn-Pd, (b) Cu-Pd, and (c) In-Pd metal particles on NBeta before and after recycling.



SI Fig. S4 Comparison of removal efficiency, selectivities and kinetics of bimetallic catalysts for NO_3^- reduction.

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