XAFS Analysis for Local Structure of Supported Catalysts -Comparison between Transmission and Fluorescence mode-

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Clay as an Catalyst Support

- **Smectite-group Materials (Cation-Exchanger)**

Montmorillonite	$Na_x(Al_{2-x}Mg_x)(Si_4O_{10})(OH)_2\cdot zH_2O$
Beidellite	$M_xAl_2(Al_xSi_{4-x}O_{10})(OH)_2\cdot zH_2O$
Hectrite	$(Na_2Ca)_{x/2}(Li_xMg_{3-x})(Si_4O_{10})(OH)_2\cdot zH_2O$
Saponite	$Ca_{x/2}Mg_3(Al_xSi_{4-x}O_{10})\cdot zH_2O$

- **Botallackite-group Materials (Anion-exchanger)**

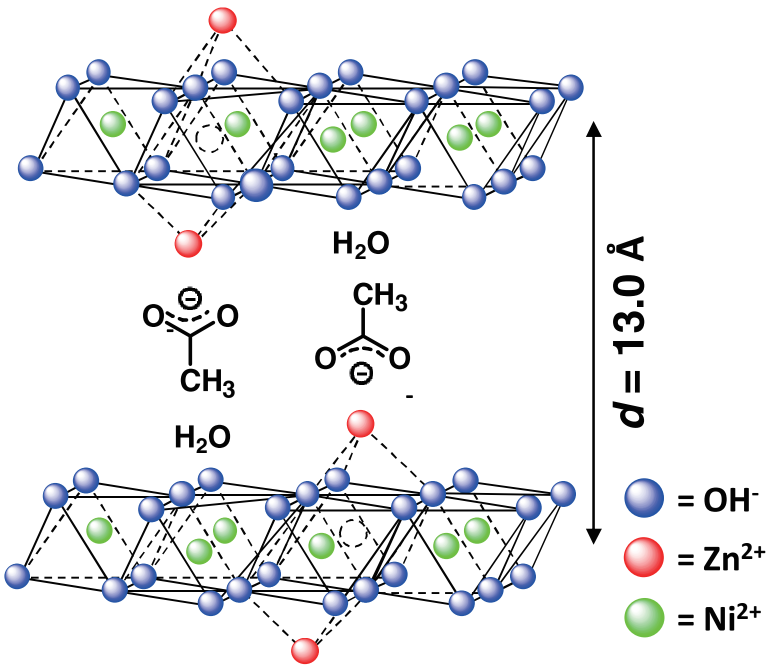
Layered Double Hydroxide: $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}Y^{z-}_{x/z}\cdot nH_2O$

Hydrotalcite	$Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$
Pyroaurite	$Mg_6Fe_2(OH)_{16}CO_3\cdot 4H_2O$
Takovite	$Ni_6Al_2(OH)_{16}CO_3\cdot 4H_2O$
Meixnerite	$Mg_6Al_2(OH)_{16}(OH)_2\cdot 4H_2O$

Layered Hydroxy Double Salt: $M^{II}_{1-x}M^{II}_{2x}(OH)_2Y^{z-}_{2x/z}\cdot nH_2O$

Layered Ni-Zn Mixed Basic Salt (NiZn)

Schematic Structure



$Ni_{1-x}Zn_{2x}(OH)_2(OAc)_{2x} \cdot nH_2O$

$(0.15 < x < 0.25)$

Ref) S. Yamanaka. *Mat. Res. Soc. Proc.* (1995)

Properties

(i) Anion exchange ability of AcO^- anion

(ii) High anion exchange capacity (2.65 $mmol/g_{NiZn}$)

(iii) Anion exchangeable sites are isolated neighboring on Zn^{2+} cation

(iV) Simple preparation

(v) Controllable clearance space

Green Alcohol Oxidation

- the clean synthesis of high value chemical intermediates -

R_1, R_2 = H, alkyl, aryl

How green is this chemical transformation?

(I) Molecular Oxygen or Air as an Oxidant

Clean, safe, low cost, and only water as a by product

(II) Heterogeneous Catalysts

Reusability and simple work-up

Utilization of multi-functions at solid surface

(III) Environmentally friendly

Reduce CO_2 emissions and preserve natural resources

Conventional Methods

Energy intensive and atom-uneconomical process

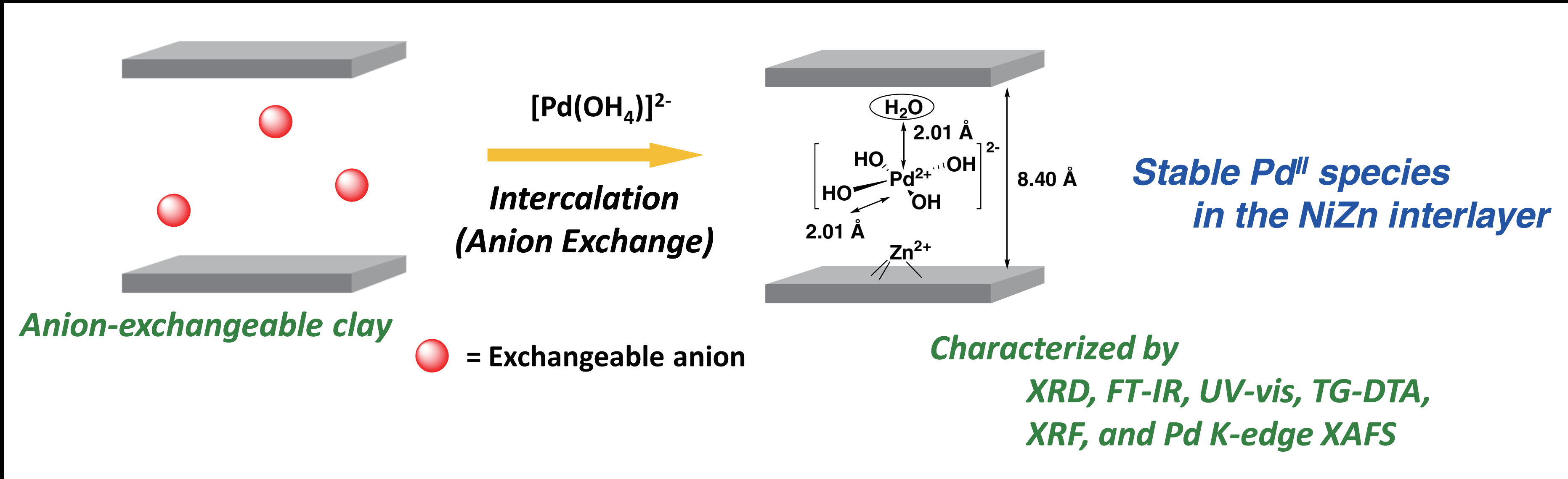
Severe reaction conditions and any additives

Stoichiometric and Hazardous Reagents

$KMnO_4$, MnO_2, $K_2Cr_2O_7$, or $CrO_3 \cdot 2C_5H_5N$, etc....

This Work

Creation of active Pd(II) species without any organic ligands stabilized by the unique features of anion-exchangeable clay materials



Advantages

(i) Stabilization of Pd(II) species with electrostatic interaction in the interlayer of clay without organic ligands

(ii) Reusability by the simple filtration or centrifugation

(iii) Weak basicity of the clay plays a key role toward successive alcohol oxidation

Preparation of Pd/NiZn Catalyst

$Ni(OAc)_2 \cdot 4H_2O$ aq. + $Zn(OAc)_2 \cdot 2H_2O$ aq.

Hydrothermal synthesis — 200 °C, 24 h

↓

NiZn

$Ni_{0.78}Zn_{0.44}(OH)_2(OAc)_{0.44} \cdot 0.86H_2O$
(Ni/Zn=1.77, C.S.=0.85 nm)
(EA, XRF and TG-DTA)

↓ *Stirred* r.t. for 3 h ← K_2PdCl_4 + NaOH aq. (*pH = 13*)

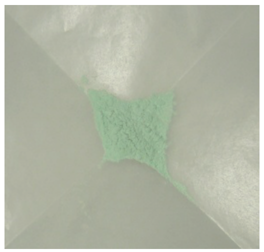
Formation of anionic $[Pd(OH)_4]^{2-}$ species (Confirmed by UV-vis)

Intercalation

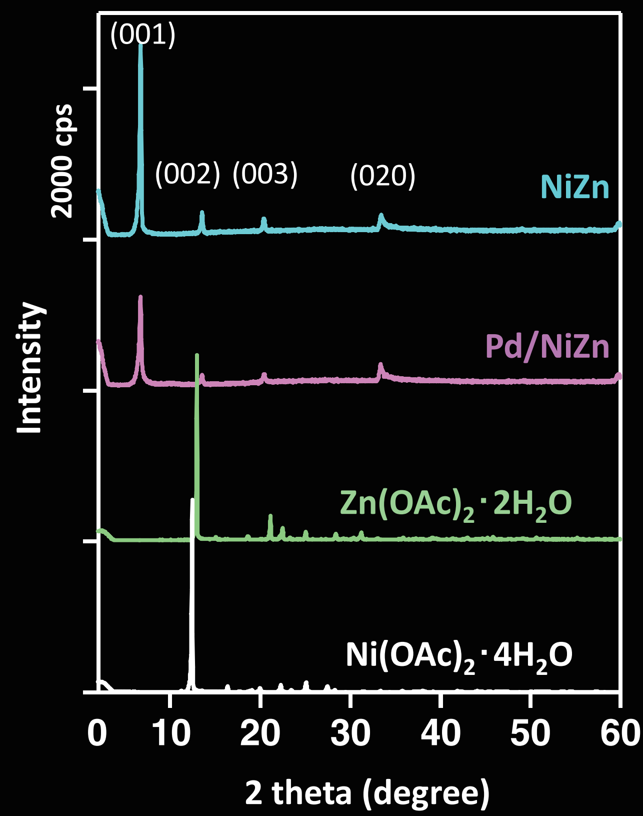
↓

Pd/NiZn

Pd loading = 0.2 wt%
(C.S. = 0.85 nm)



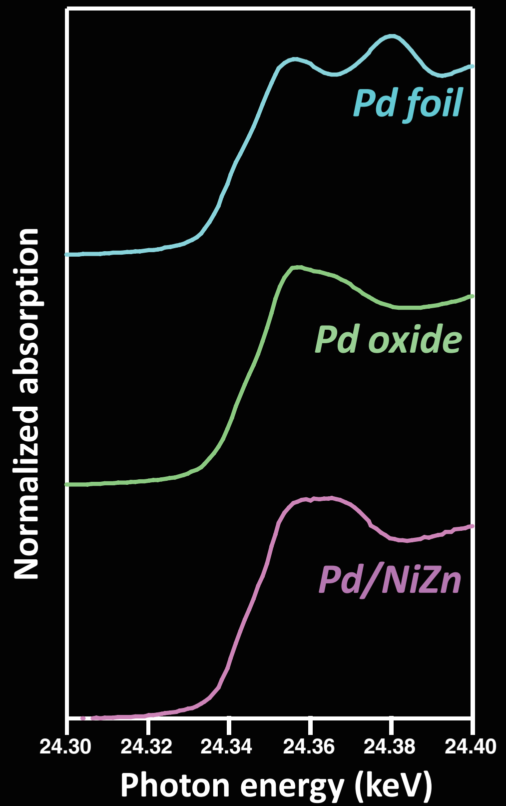
XRD Profiles



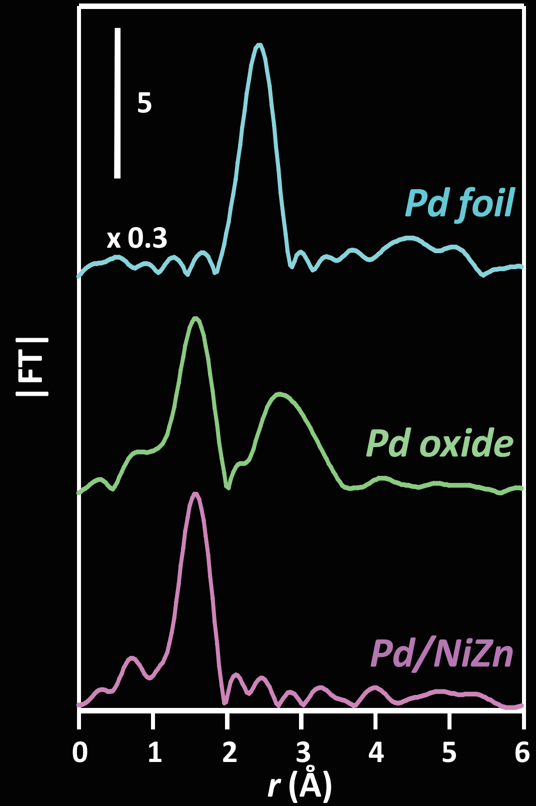
No structural change of NiZn was observed by intercalating the Pd species.

Local Structure of Pd Species in Pd/NiZn (0.2 wt%)

Pd K-edge XANES

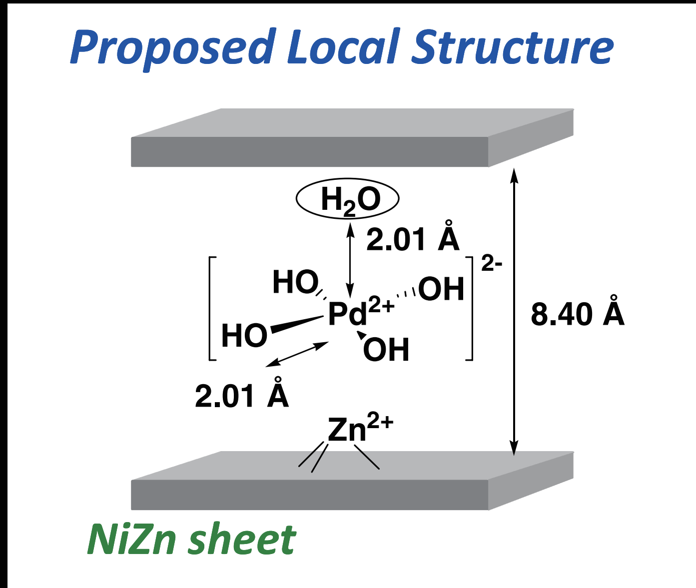


FT of Pd K-edge EXAFS



XAFS analysis:

Fluorescence mode
using Lytle detector
at PF-AR NW-10A
(Proposal No. 2007G662)



Curve-fitting Analysis[a]

sample	shell	CN [b]	r (Å) [c]	σ (Å) [d]
Pd foil [e]	Pd-Pd	(12)	(2.74)	
PdO [e]	Pd-O	(4)	(2.02)	
	Pd-(O)-Pd	(4)	(3.03)	
	Pd-(O)-Pd	(8)	(3.42)	
Pd/NiZn	Pd-O	5.16	2.01	0.0476

[a] Inverse Fourier transformations were performed for the regions of 1.16-1.96 Å of the Pd/NiZn.
[b] Coordination number. [c] Bond distance. [d] σ^2 is Debye-Waller factors. [e] Data from X-ray crystallography.

Monomeric Pd^{II} species is successfully intercalated via anion exchange process!

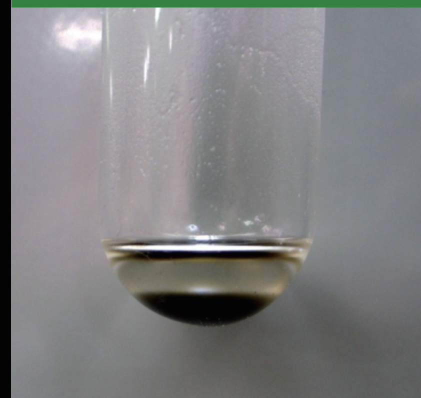
Benzylalcohol Oxidation Under Various Conditions[a]

entry	catalyst	solvent	conv. (%)[b]	yield (%)[b]
1	Pd/NiZn	$PhCF_3$	99	97
2[c]	Pd/NiZn	$PhCF_3$	99	99
3[d]	Pd/NiZn	$ChCF_3$	trace	trace
4	Pd/NiZn	$ClCH_2CH_2Cl$	81	79
5	Pd/NiZn	*n*-heptane	79	71
6	Pd/NiZn	EtOAc	58	50
7	Pd/NiZn	MeCN	47	42
8	Pd/NiZn	DMF	trace	trace
9	Pd/NiZn	DMSO	trace	trace
10	Pd/NiZn	EtOH	trace	trace
11	Pd/NiZn	water	47	41
12	NiZn	$PhCF_3$	ttrace	trace
13	none	$PhCF_3$	No Reaction	
14[e]	Pd/Hydrotalcite	$PhCF_3$	>99	>99

[a] Benzyl alcohol (0.5 mmol), Pd catalyst (Pd: 2 mol%), solvent (2.5 mL), 80 °C, O_2 atmosphere. [b] Determined by GC analysis using an internal standard technique. [c] The catalytic reaction was carried out under 1 atm of air instead of pure O_2. [d] N_2 atmosphere. [e] Hydrotalcite, $Mg_6Al_2(OH)_{16}(CO_3)$, was purchased from Tomita Pharm.

Pd/NiZn

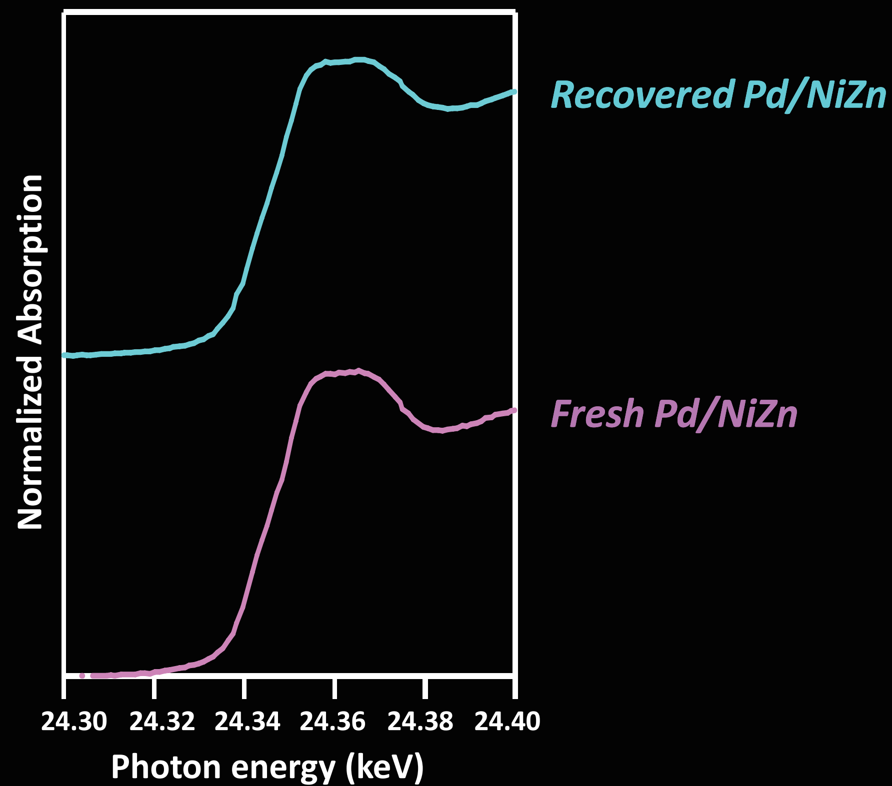
Pd/Hydrotalcite



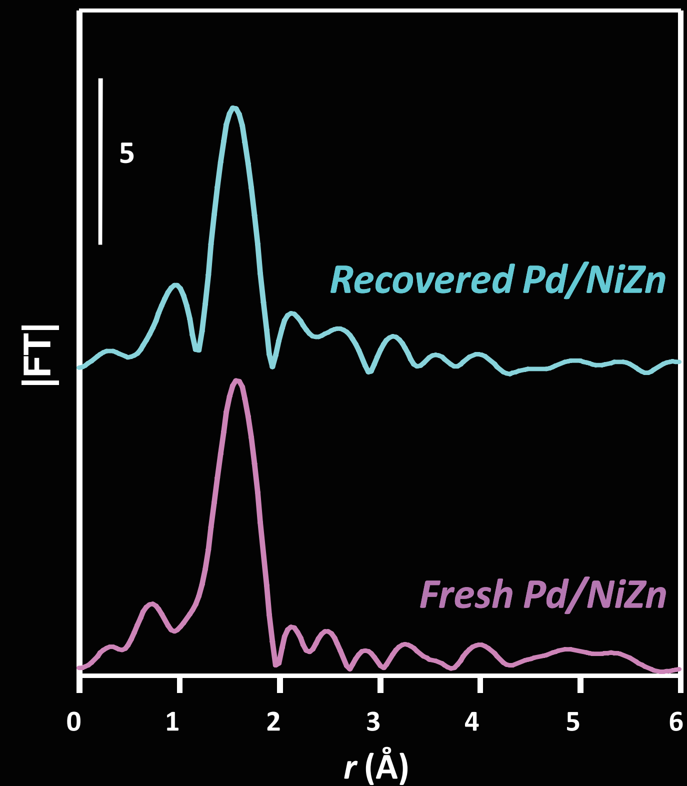
Pd/Hydrotalcite catalyst was changed into black color.

Stable Pd^{II} Species in the NiZn Interlayer

Pd K-edge XANES



FT of Pd K-edge EXAFS



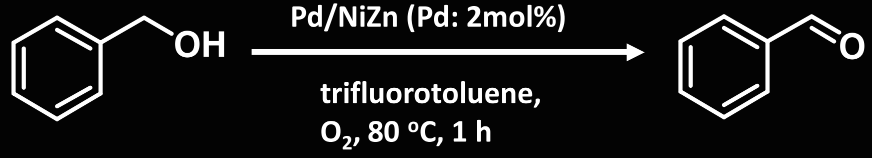
Curve-fitting Analysis[a]

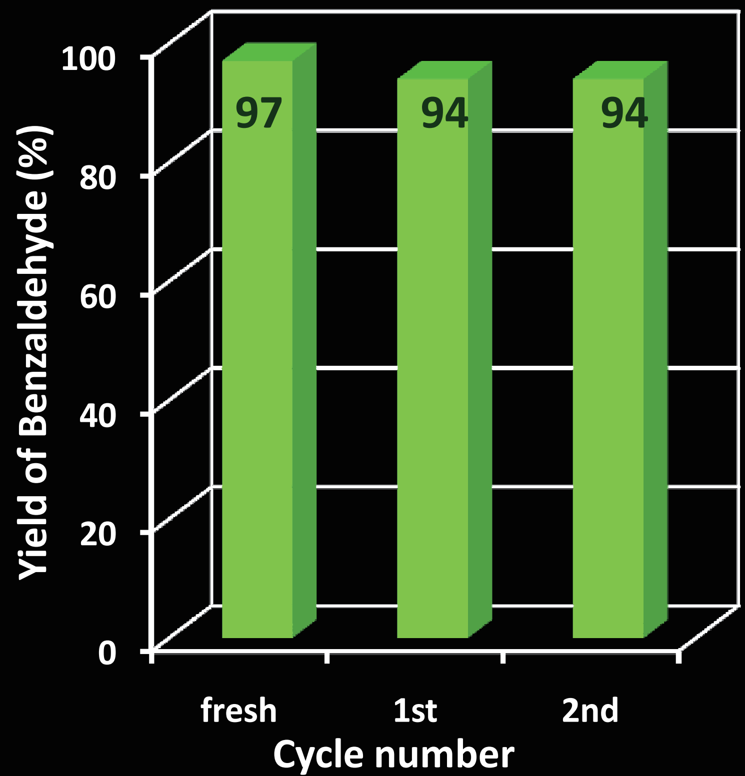
sample	shell	CN [b]	*r* (Å) [c]	σ (Å) [d]
Fresh Pd/NiZn	Pd-O	5.16	2.01	0.0476
Recovered Pd/NiZn	Pd-O	5.14	2.01	0.0325

[a] Inverse Fourier transformations were performed for the regions of 1.16-1.96 Å of the Pd/NiZn.
[b] Coordination number. [c] Bond distance. [d] σ^2 is Debye-Waller factors.

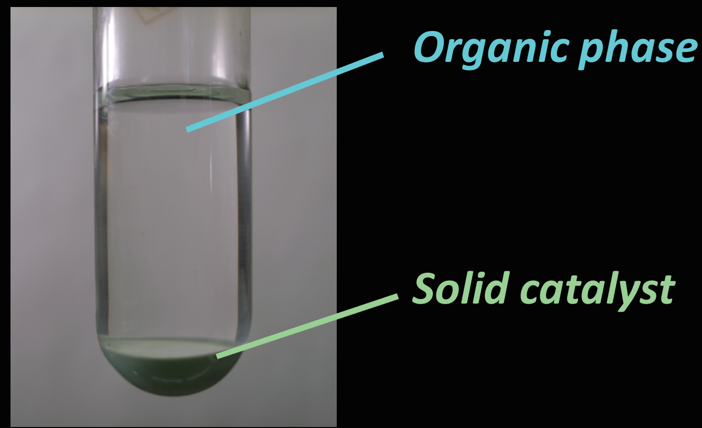
Pd species in Pd/NiZn catalyst keeps its original structure even after catalytic reaction due to the strong interaction between anionic Pd(II) species and the layered host.

Reuse Experiment



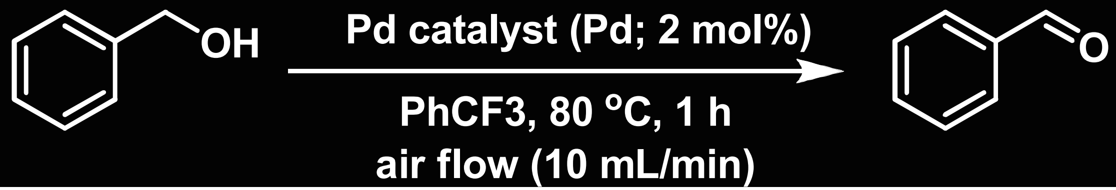


After simple centrifugation



The Pd/NiZn catalyst could be reused without any loss of its activity and selectivity!

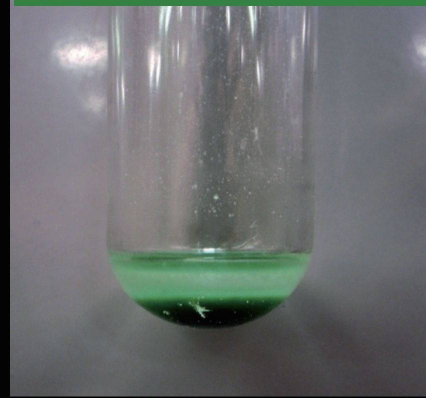
Benzylalcohol Oxidation Under Various Conditions[a]



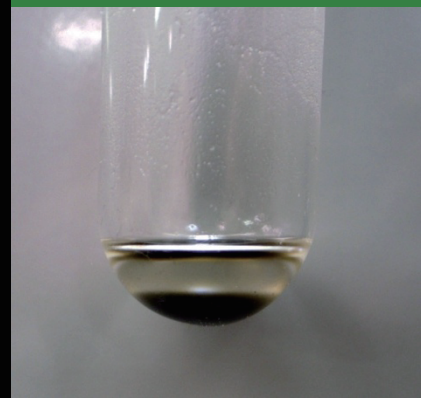
Entry	Catalyst	Convn (%)[b]	Yield (%)[b]
1	Pd/NiZn(0.2)	>99	97
2[c]	Pd/NiZn(0.2)	>99	99
3[d]	Pd/NiZn(0.2)	4	2
4	Pd/HT(0.2)	>99	>99
5	Pd/NiZn(10)	7	6
6[e]	Pd/NiZn(0.2)	98	94
7[f]	Pd/NiZn(0.2)	>99	94
8[g]	NiZn	0	0
9	none	0	0

[a] Benzyl alcohol (0.5 mmol), Pd catalyst (Pd: 2 mol%), $PhCF_3$ (2.5 mL), 80 °C, 1 h, air flow (10 mL/min). HT, $Mg_6Al_2(OH)_{16}(CO_3)$, was purchased from Tomita Pharm. [b] Determined by GC analysis using an internal standard technique. [c] Under 1 atm of O_2. [d] Under 1 atm of N_2. [e] 1st recycle. [f] 2nd recycle. [g] NiZn (0.5 g) was used as a catalyst.

Pd/NiZn(0.02)

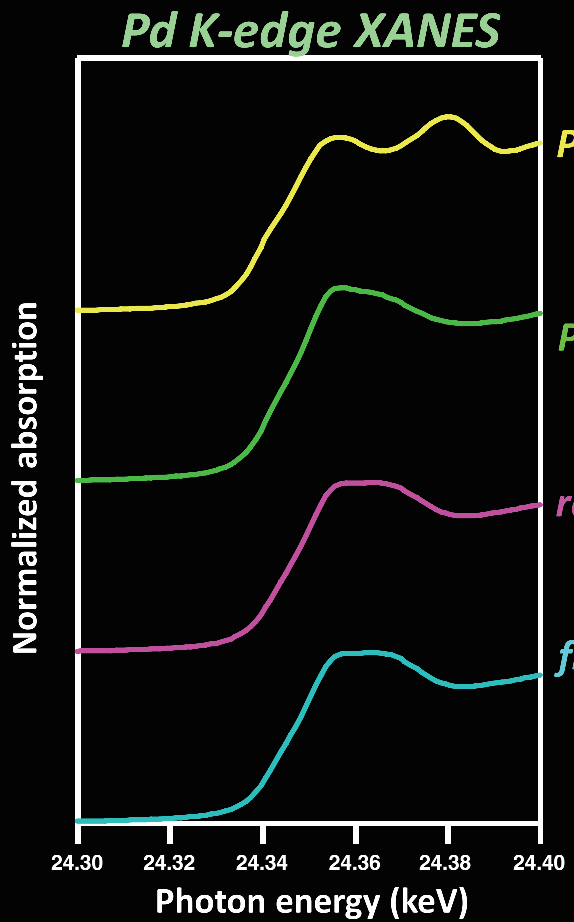


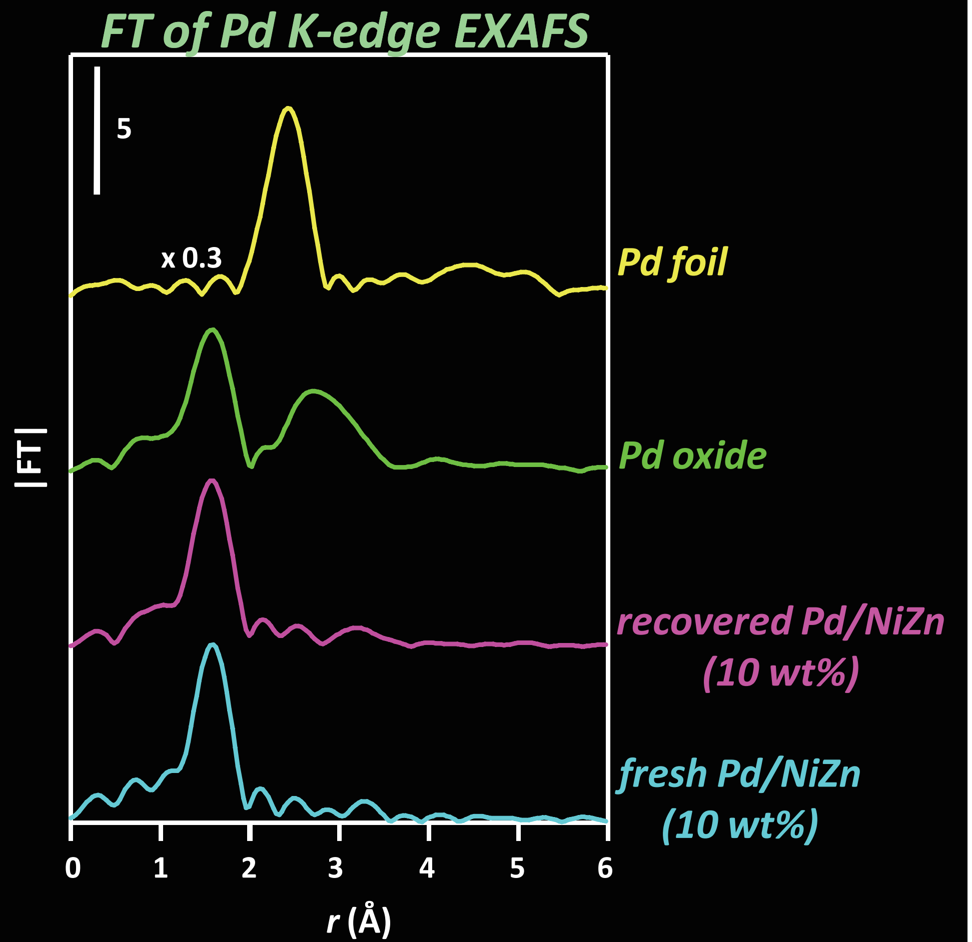
Pd/Hydrotalcite



Pd/Hydrotalcite catalyst was changed into black color.

Characterization of Pd/NiZn Catalyst (Pd: 10 wt%)





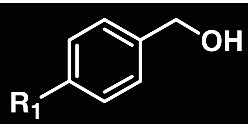
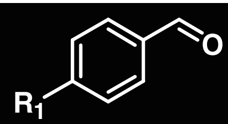
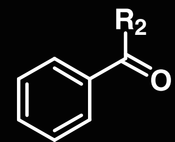
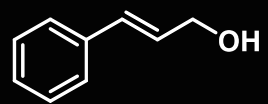
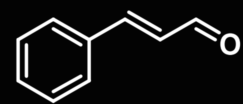
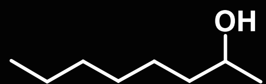
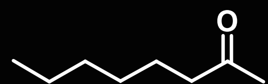
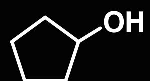
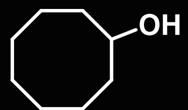
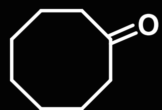
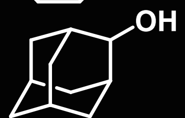
Curve-fitting Analysis[a]

sample	shell	CN [b]	r (Å) [c]	σ (Å) [d]
Fresh Pd/NiZn	Pd-O	4.41	2.02	0.054
Recovered Pd/NiZn	Pd-O	4.13	2.02	0.013

[a] Inverse Fourier transformations were performed for the regions of 1.16-1.96 Å of the Pd/NiZn.
[b] Coordination number. [c] Bond distance. [d] σ^2 is Debye-Waller factors.

This is the first demonstration of creating highly stable monomeric Pd species even in high Pd loading due to the strong interaction between anionic Pd(II) species and the layered host.

Alcohol Oxidation Under 1 atm of Air[a]

entry	substrate	time (h)	product	conv. (%)[b]	yield (%)[b]
					
1	R_1 = H	1	R_1 = H	99	99
2	CH_3	0.5	CH_3	>99	>99
3	OCH_3	0.5	OCH_3	>99	>99
					
4	R_2 = CH_3	1	R_2 = CH_3	>99	99
5	cyclopropyl	10	cyclopropyl	85	81
6	Ph	12	Ph	92	90
7		2		>99	71
8		24		>99	>99
9		24		98	98
10		12		90	85
11		12		98	97
12		12		>99	96

[a] Alcohol (0.5 mmol), Pd/NiZn (Pd: 2 mol%), TFT (2.5 mL), 80 °C, air flow (20 mL/min).
[b] Determined by GC analysis using an internal standard technique.

Wide range of alcohols were converted into the corresponding carbonyl compounds with Pd/NiZn catalyst under air atmosphere.

NiZn-intercalated Anionic Rh Hydroxyl Complex Catalyst

NiZn

$Ni_{0.78}Zn_{0.44}(OH)_2(OAc)_{0.44}\cdot 0.86H_2O$

(Ni/Zn=1.77, C.S.=0.85 nm)

Ni: 30.5 wt%, Zn: 19.2 wt%

(EA, XRF and TG-DTA)

$Na_3RhCl_6\cdot 12H_2O$ + NaOH

pH = 14

Stirred at r.t. for 12 h

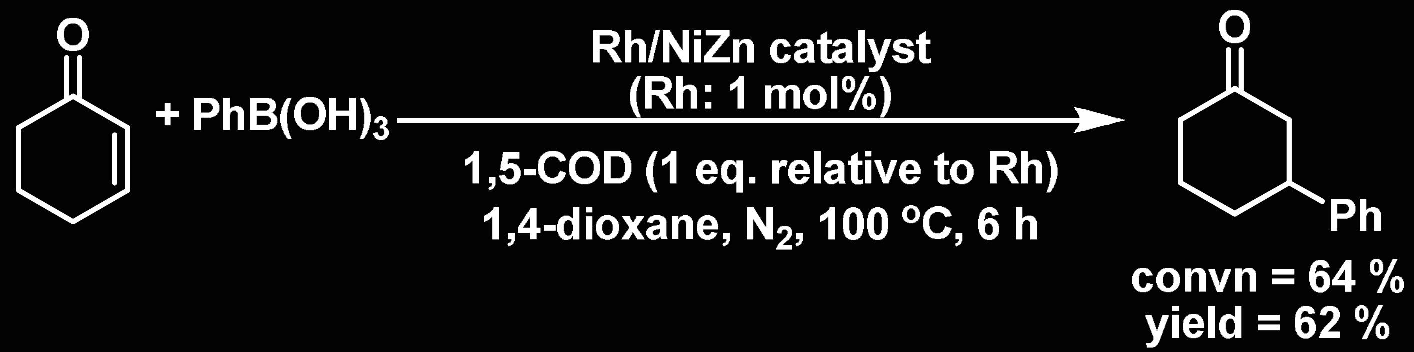
→

Rh/NiZn

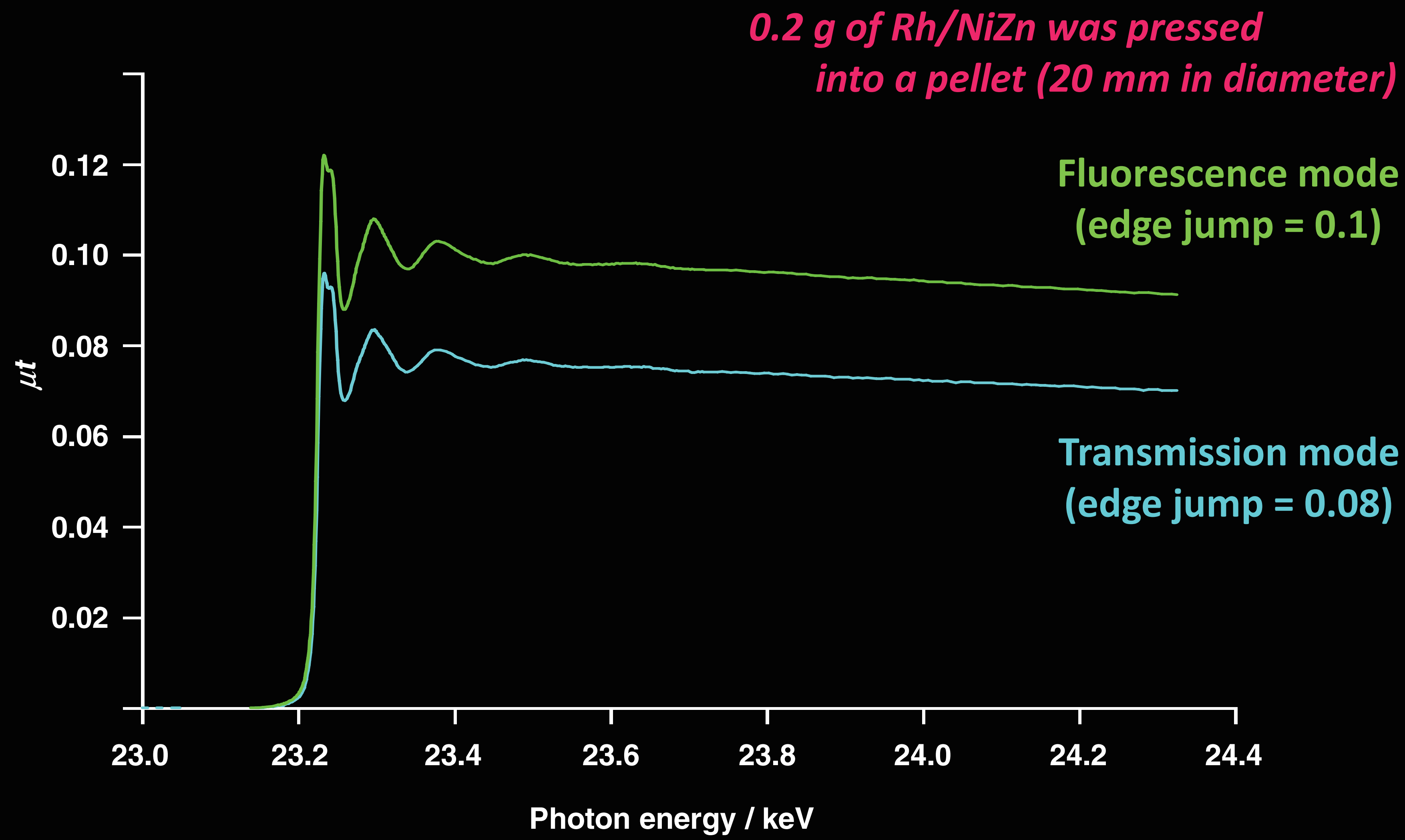
Rh loading = 1 wt%

(C.S. = 0.36 nm)

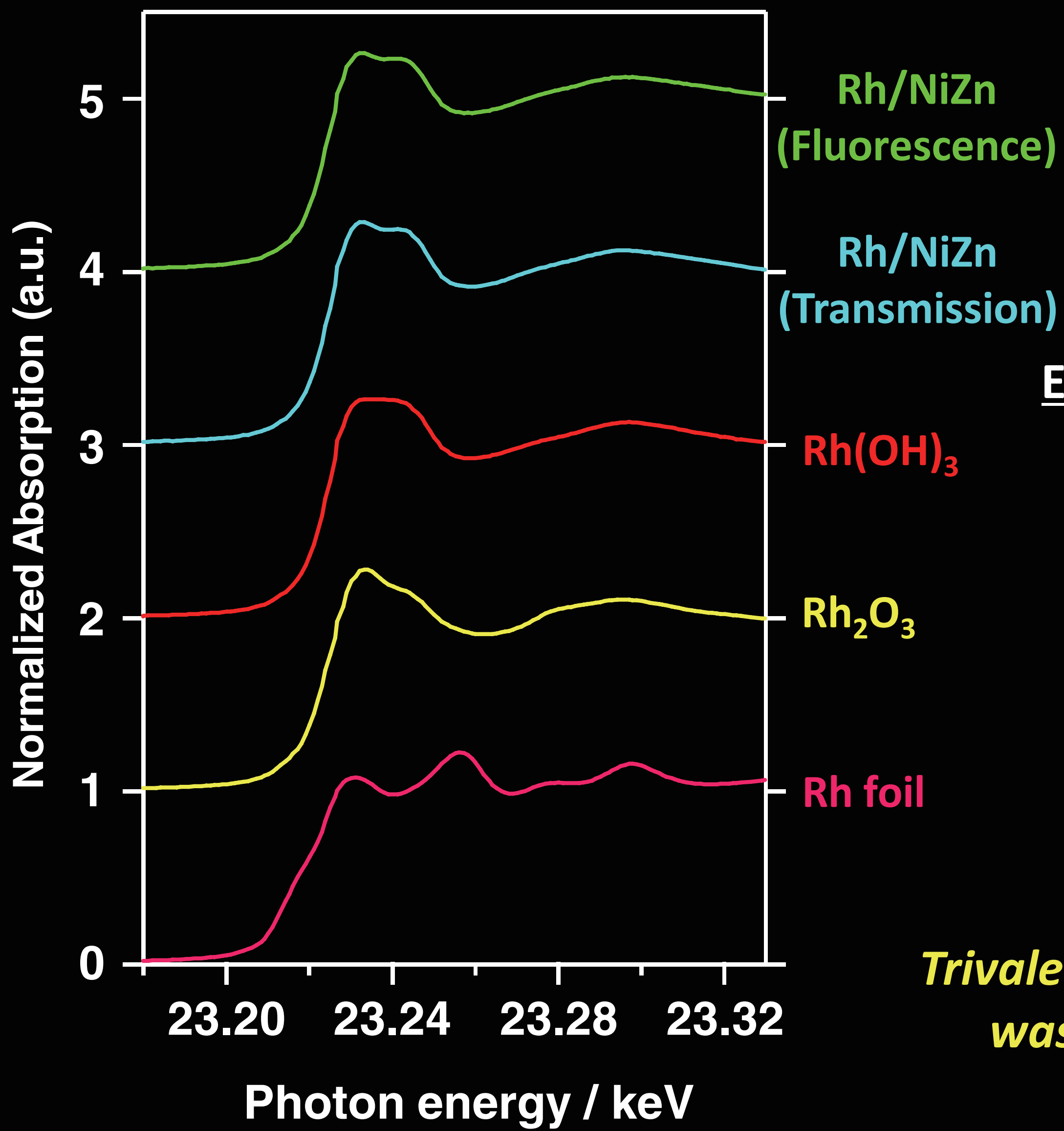
Rh/NiZn Catalyzed 1,4-Addition between Organoboron and Enones



Comparison Between Transmission and Fluorescence Mode
- Rh K-edge XAFS for Rh/NiZn Catalyst -



Comparison Between Transmission and Fluorescence Mode
- Rh K-edge XANES -



The shape of Rh/NiZn was similar to $Rh(OH)_3$.

<u>E_0 value:</u>

Rh foil: 23223.918 eV

Rh_2O_3: 23226.127 eV

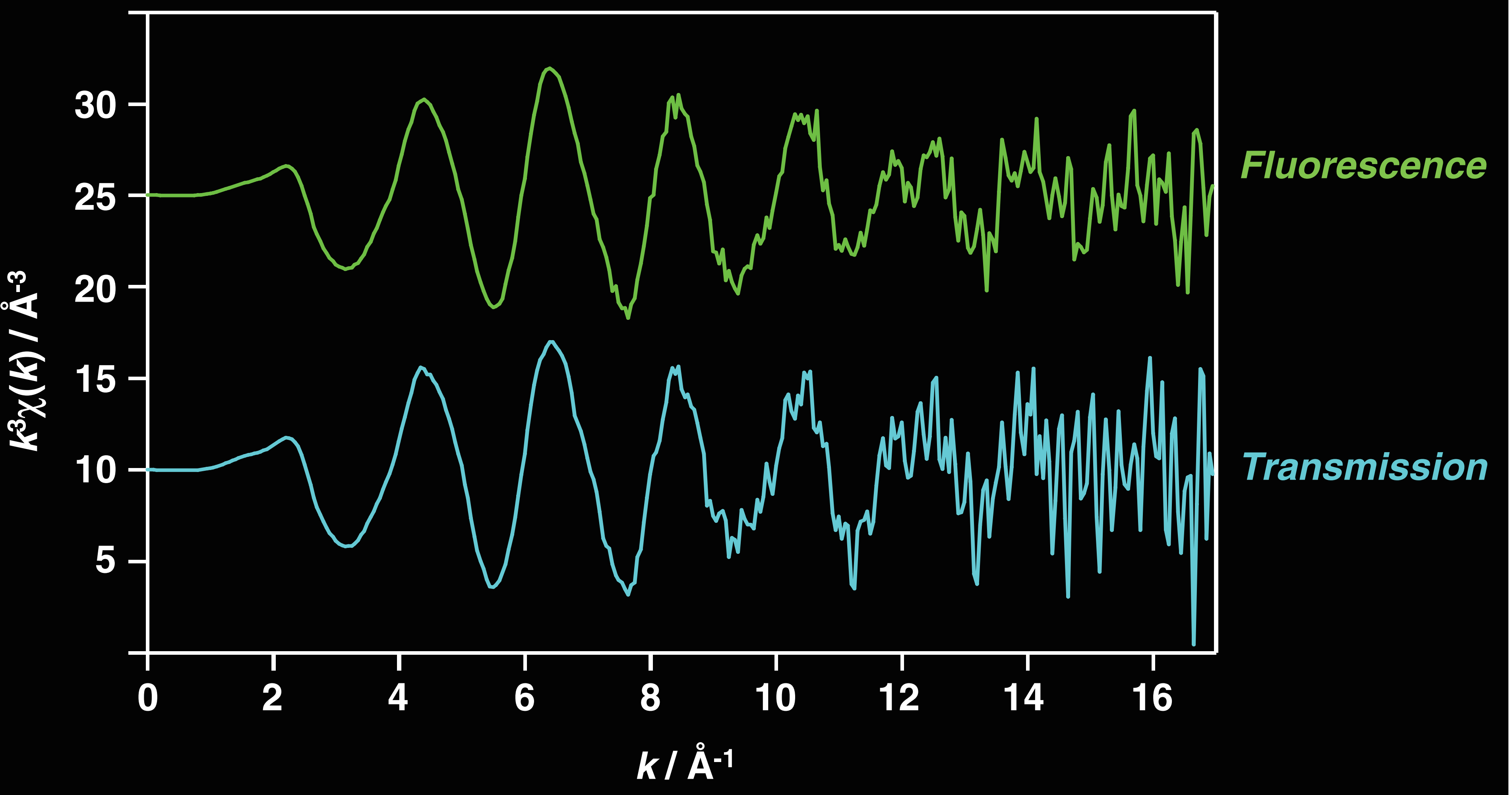
$Rh(OH)_3$: 23224.900 eV

Rh/NiZn (trans): 23224.900 eV

Rh/NiZn (fluor): 23225.145 eV

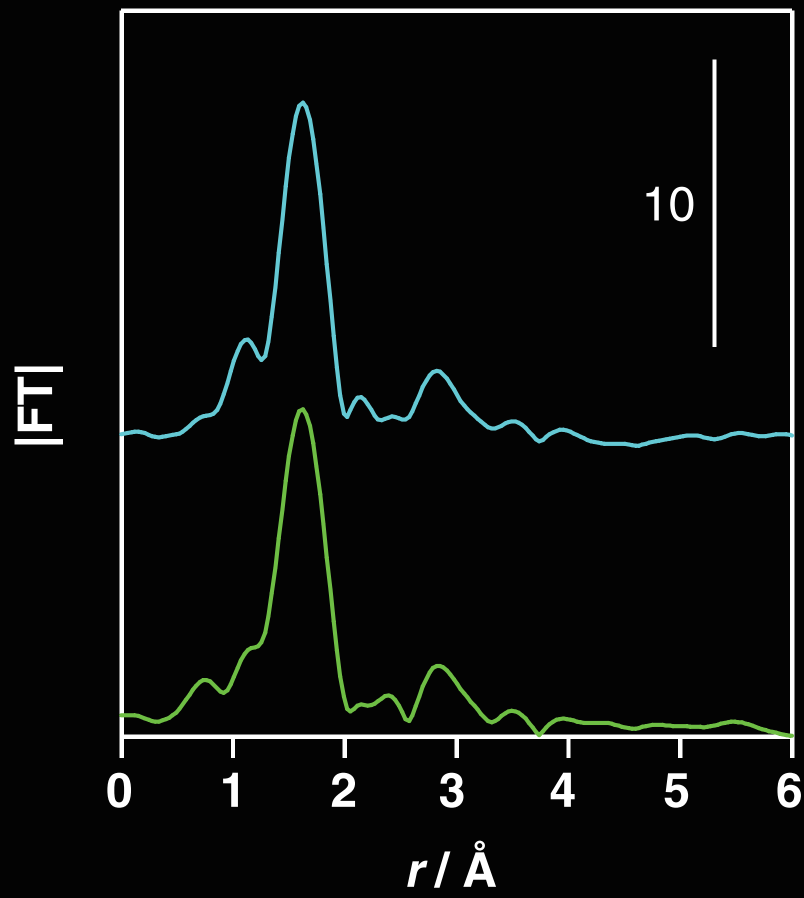
Trivalent anionic Rh species was successfully intercalated into the NiZn interlayer.

Comparison Between Transmission and Fluorescence Mode
- k^3-weighted Rh K-edge EXAFS Spectra -



Comparison Between Transmission and Fluorescence Mode
- FT and Curve-fitting Analysis -

FT of Rh K-edge EXAFS



Curve-fitting Results

Mode	Shell	C.N.[b]	r (Å) [c]	σ (Å) [d]
Trans	Rh-O	5.5	2.05	0.051
Fluore	Rh-O	5.8	2.05	0.057

[a] Inverse Fourier transformations were performed for the regions of 1.26-2.03 Å of the Rh/NiZn.
[b] Coordination number.
[c] Bond distance.
[d] σ is Debye-Waller factors.