



Promoting effect of MgO addition to Pt/Ni/CeO₂/Al₂O₃ in the steam gasification of biomass

著者	Nakamura Kazuya, Miyazawa Tomohisa, Sakurai Takuya, Miyao Toshihiro, Naito Shuichi, Begum Noorjahan, Kunimori Kimio, Tomishige Keiichi
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Table 1. Properties of the catalysts after H₂ pretreatment at 773K.

catalysts	BET surface area / m ² ·g ⁻¹ -cat	H ₂ consumption ^{a)} / 10 ⁻³ mol·g ⁻¹ -cat	Ni-based reduction degree ^{b)} / %	H ₂ adsorption ^{c)} / 10 ⁻⁵ mol·g ⁻¹ -cat	Dispersion ^{d)} / %	Particle size of Ni metal ^{e)} / nm
Ni/CA	17.4	1.40	89	4.1	5.9	16.6
Pt/Ni/CA	18.8	1.51	96	4.2	5.6	17.5
Ni/CMA	17.6	0.46	29	4.1	17.8	5.4
Pt/Ni/CMA	19.2	0.47	30	3.9	16.6	5.9
Ni/MA	9.0	0.16	10	2.6	32.5	3.0
Pt/Ni/MA	9.1	0.24	15	2.4	20.0	4.9

a) H₂ consumption below 773 K in TPR profiles shown in Figure 3.

b) Based on the assumption that $\text{Ni}^{2+} + \text{H}_2 \rightarrow \text{Ni}^0 + 2\text{H}^+$, and the reduction of Pt and CeO₂ was neglected.

c) H₂ adsorption is total adsorption at room temperature, and H/Ni = 1 is assumed.

d) $2 \times (\text{H}_2 \text{ adsorption}) / (\text{H}_2 \text{ consumption}) \times 100$.

e) Particle size of Ni metal is calculated by the relation: $(\text{particle size} / \text{nm}) = 9.71 / (\text{dispersion} / \%) \times 10$.

Table 2. Curve fitting results of Ni *K*-edge EXAFS of the Pt/Ni/CA and Pt/Ni/CMA catalysts.

Catalyst	Condition	Shells	CN ^{a)}	$R / 10^{-1} \text{ nm}^{\text{b)}$	$\sigma / 10^{-1} \text{ nm}^{\text{c)}$	$\Delta E_0 / \text{eV}^{\text{d)}$	$R_f / \%^{\text{e)}$
Pt/Ni/CA	reduction	Ni-Ni	10.4±1.5	2.49±0.008	0.073±0.012	-0.5±2.0	0.1
	reaction	Ni-Ni	6.8±1.0	2.49±0.009	0.076±0.012	-5.0±2.0	0.6
	regeneration	Ni-Ni	10.7±1.6	2.49±0.008	0.072±0.012	-0.7±2.0	0.1
Pt/Ni/CMA	reduction	Ni-O	2.1±0.2	2.10±0.007	0.060±0.009	-2.4±0.5	0.9
		Ni-Ni	8.5±0.1	2.49±0.003	0.077±0.001	-1.1±0.1	
		Ni-O-Ni	2.8±0.3	2.93±0.005	0.068±0.013	8.5±0.5	
		Ni-O-Mg	1.4±0.4	2.94±0.018	0.069±0.017	3.4±1.4	
	reaction	Ni-O	1.8±0.2	2.10±0.009	0.072±0.018	-4.7±1.9	0.5
		Ni-Ni	9.1±0.1	2.49±0.001	0.069±0.001	-1.1±0.1	
		Ni-O-Ni	2.3±0.1	2.93±0.004	0.071±0.005	8.0±0.6	
		Ni-O-Mg	1.3±0.2	2.94±0.000	0.071±0.019	-5.3±1.7	
	regeneration	Ni-O	2.1±0.8	2.10±0.018	0.068±0.013	-3.3±1.7	0.9
		Ni-Ni	8.6±0.1	2.49±0.000	0.077±0.001	-0.9±0.2	
		Ni-O-Ni	2.7±0.1	2.93±0.006	0.063±0.004	6.7±0.6	
		Ni-O-Mg	1.4±0.5	2.94±0.017	0.061±0.020	5.1±1.6	
Ni foil	-	Ni-Ni	12	2.49	0.060	0.0	-
NiO	-	Ni-O	6	2.10	0.060	0.0	-
	-	Ni-O-Ni	12	2.94	0.060	0.0	

a) Coordination number. b) Bond distance. c) Debye-Waller factor. d) Difference in the origin of photoelectron energy between the reference and the sample. e) Residual factor.

Fourier transform range: 30-160 nm⁻¹, Fourier filtering range: 0.126-0.292 nm.

Figure 1. Catalytic performance in steam gasification of cedar wood over the catalysts after H₂ reduction.

Conditions: biomass; 60 mg/min (H₂O 9.2 %, C 2191 μmol/min; H 3543 μmol/min; O 1475 μmol/min), N₂ flow rate; 60 ml/min, (added H₂O)/C=0.5 (steam flow rate 1110 μmol/min), reaction time; 15min, H₂ reduction 773 K, 30 min.

Figure 2. Catalytic performance in steam gasification of cedar wood over the catalysts after H₂ reduction.

Conditions: biomass; 60 mg/min (H₂O 9.2 %, C 2191 μmol/min; H 3543 μmol/min; O 1475 μmol/min), N₂ flow rate; 60 ml/min, (added H₂O)/C=0.5 (steam flow rate 1110 μmol/min), reaction time; 15 min, H₂ reduction 773 K, 30 min.

Figure 3. Catalytic performance in steam gasification of cedar wood at 923 K as a function of time on stream over the catalysts without H₂ reduction.

(a) Pt/Ni/CA (b) Pt/Ni/CMA

Conditions: biomass; 60 mg/min (H₂O 9.2 %, C 2191 μmol/min; H 3543 μmol/min; O 1475 μmol/min), N₂ flow rate; 60 ml/min, (added H₂O)/C=0.5 (steam flow rate 1110 μmol/min).

Figure 4. TPR profiles of the catalysts.

(a) Pt/Ni/CA (b) Ni/CA (c) Pt/Ni/CMA (d) Ni/CMA (e) Pt/Ni/MA (f) Ni/MA

TPR condition: heating rate 10 K/min, Room temperature to 1273 K, and the temperature was maintained at 1273 K for 30 min. 5 % H₂/Ar flow rate 30 ml/min.

Sample weight: 200 mg.

Figure 5. TEM images of the catalysts after H₂ pretreatment at 773K.

(a) Pt/Ni/CA (b) Pt/Ni/CMA

Figure 6. Catalytic performance in steam gasification of cedar wood as a function of time on stream over the catalysts at 923 K.

(a) Pt/Ni/CA (b) Pt/Ni/CMA

Conditions: biomass; 60 mg/min (H₂O 9.2 %, C 2191 μmol/min; H 3543 μmol/min; O 1475 μmol/min), N₂ flow rate; 60 ml/min, (added H₂O)/C=0.5 (steam flow rate 1110 μmol/min), H₂ reduction at 773 K, 30 min.

Figure 7. Catalytic performance in steam gasification of cedar wood as a function of time on stream over the catalysts at 873 K.

(a) Pt/Ni/CA (b) Pt/Ni/CMA

Conditions: biomass; 60 mg/min (H₂O 9.2 %, C 2191 μ mol/min; H 3543 μ mol/min; O 1475 μ mol/min), N₂ flow rate; 60 ml/min, (added H₂O)/C=1 (steam flow rate 2220 μ mol/min), H₂ reduction at 773 K, 30 min.

Figure 8. XRD patterns of Pt/Ni/CA (I) and Pt/Ni/CMA (II).

■ = Ni, ● = CeO₂, ▲ = Al₂O₃

(a) After H₂ reduction, (b) after the reaction at 923 K (Figure 6), (c) after the regeneration.

Figure 9. Results of Ni *K*-edge EXAFS analysis of Pt/Ni/CA.

(a) After H₂ reduction, (b) after the reaction at 923 K (Figure 6), (c) after the regeneration.

I: k^3 -weighted EXAFS oscillation.

II: Fourier transform of k^3 -weighted Ni *K*-edge EXAFS. FT range : 30-160 nm⁻¹.

III: Fourier filtered EXAFS data (solid line) and calculated data (dotted line).

Fourier filtering range : 0.126 - 0.292 nm.

Figure 10. Results of Ni *K*-edge EXAFS analysis of Pt/Ni/CMA.

(a) After H₂ reduction, (b) after the reaction at 923 K (Figure 6), (c) after the regeneration.

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II: Fourier transform of k^3 -weighted Ni *K*-edge EXAFS. FT range : 30-160 nm⁻¹.

III: Fourier filtered EXAFS data (solid line) and calculated data (dotted line).

Fourier filtering range : 0.126 - 0.292 nm.

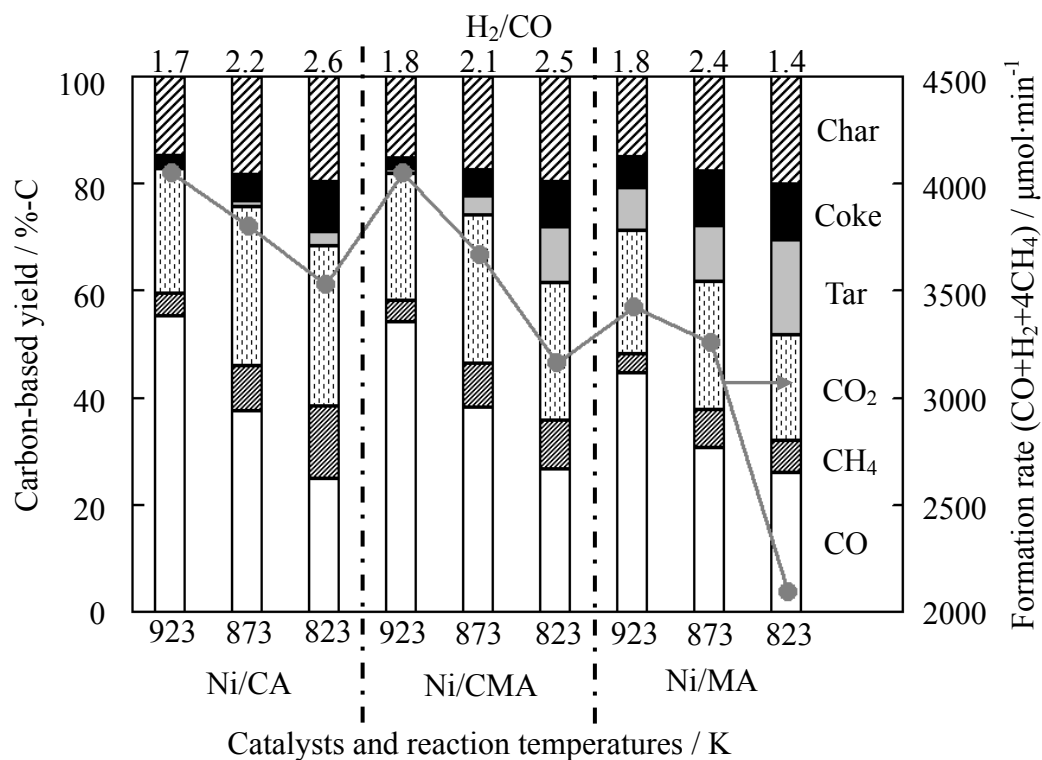


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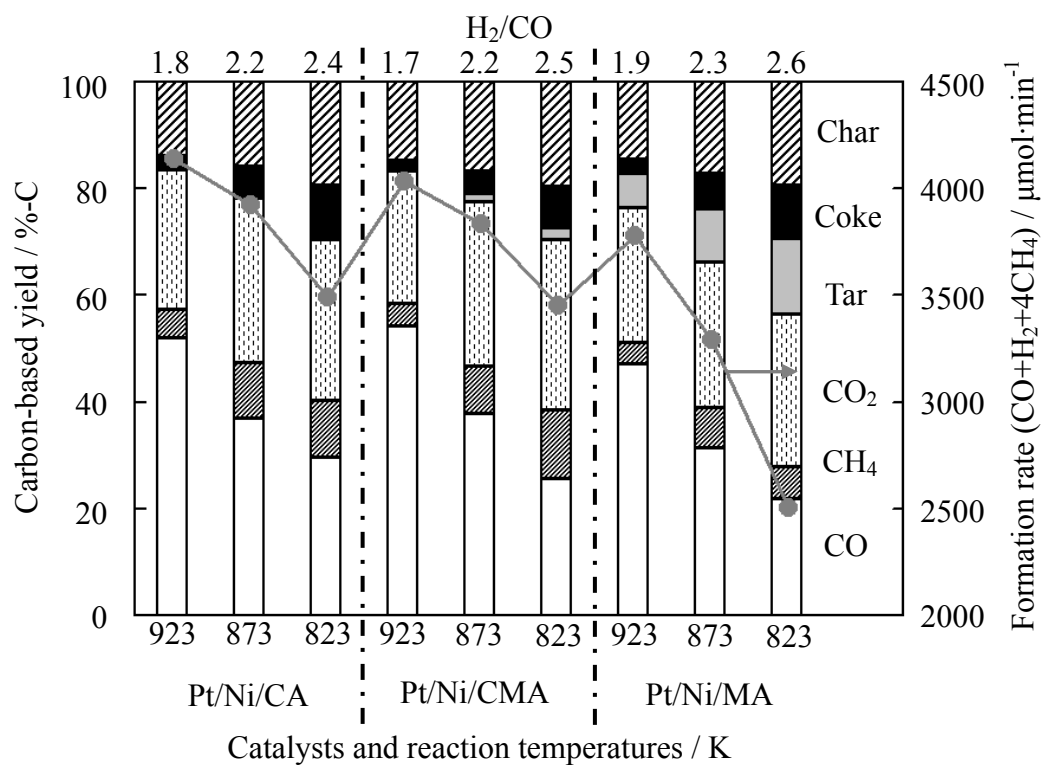


Figure 2. Catalytic performance in steam gasification of cedar wood over the catalysts after H₂ reduction.

Conditions: biomass; 60 mg/min (H₂O 9.2 %, C 2191 μmol/min; H 3543 μmol/min; O 1475 μmol/min), N₂ flow rate; 60 ml/min, (added H₂O)/C=0.5 (steam flow rate 1110 μmol/min), reaction time; 15 min, H₂ reduction 773 K, 30 min.

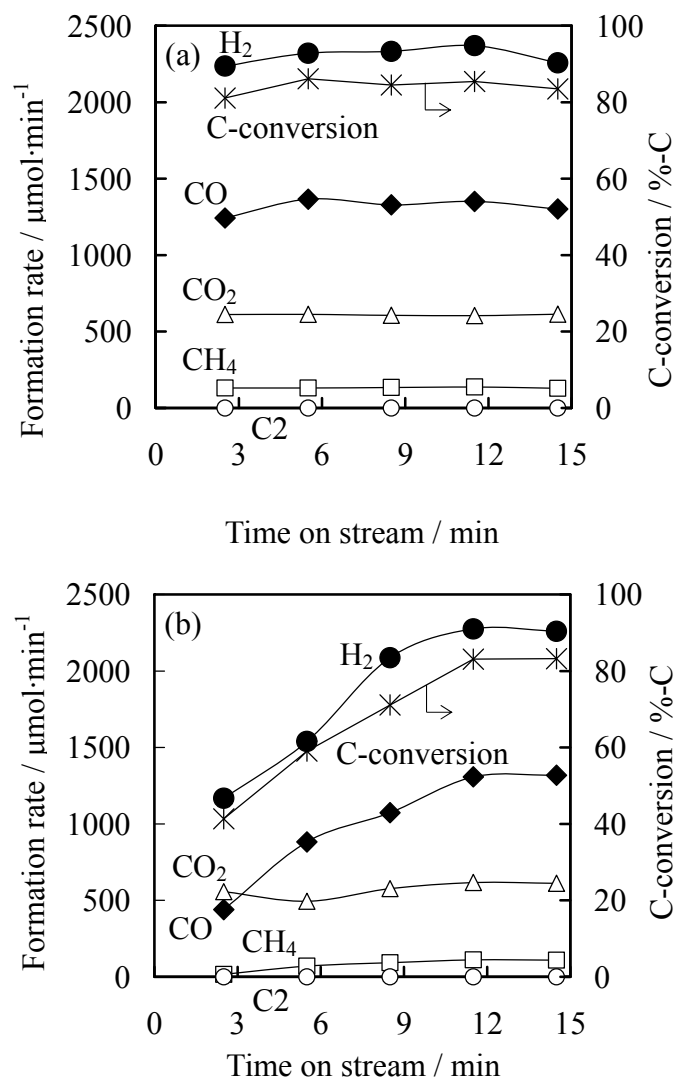


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Conditions: biomass; 60 mg/min (H₂O 9.2 %, C 2191 μmol/min; H 3543 μmol/min; O 1475 μmol/min), N₂ flow rate; 60 ml/min, (added H₂O)/C=0.5 (steam flow rate 1110 μmol/min).

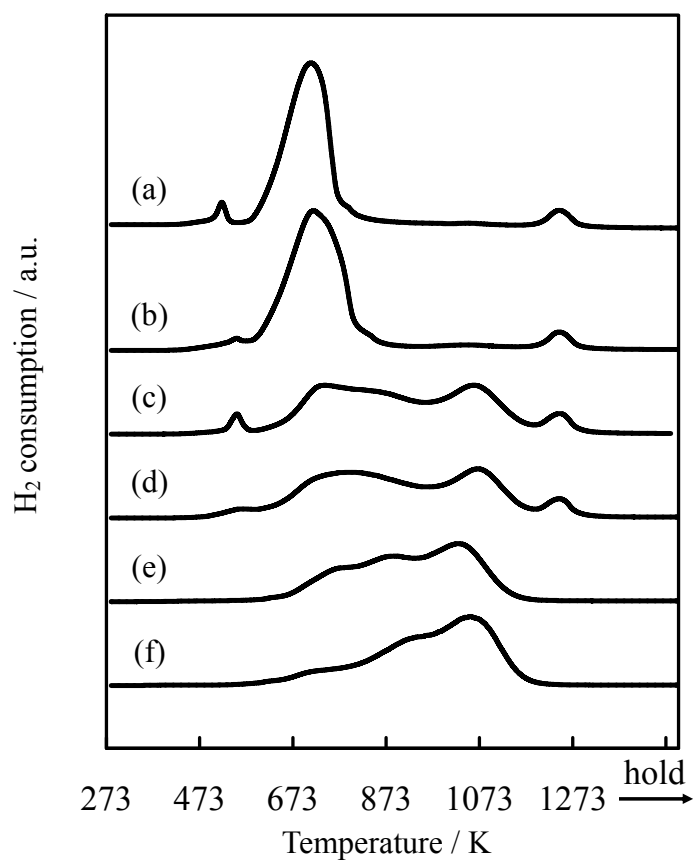


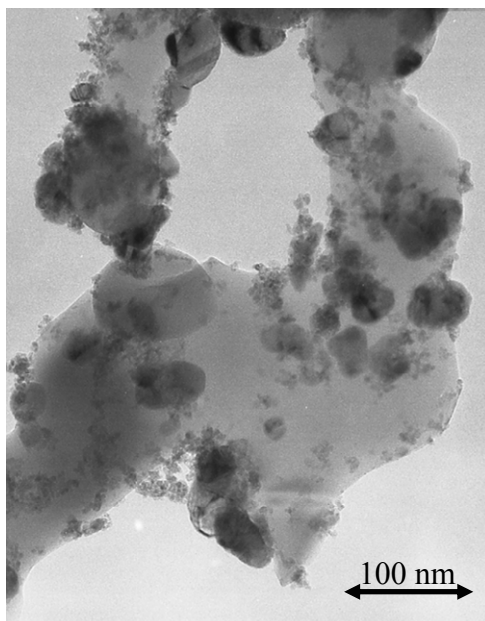
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TPR condition: heating rate 10 K/min, Room temperature to 1273 K, and the temperature was maintained at 1273 K for 30 min. 5 % H₂/Ar flow rate 30 ml/min.

Sample weight: 200 mg.

(a)



(b)

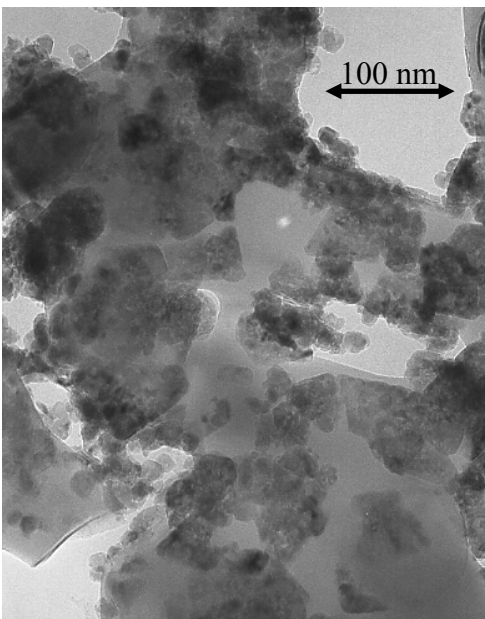


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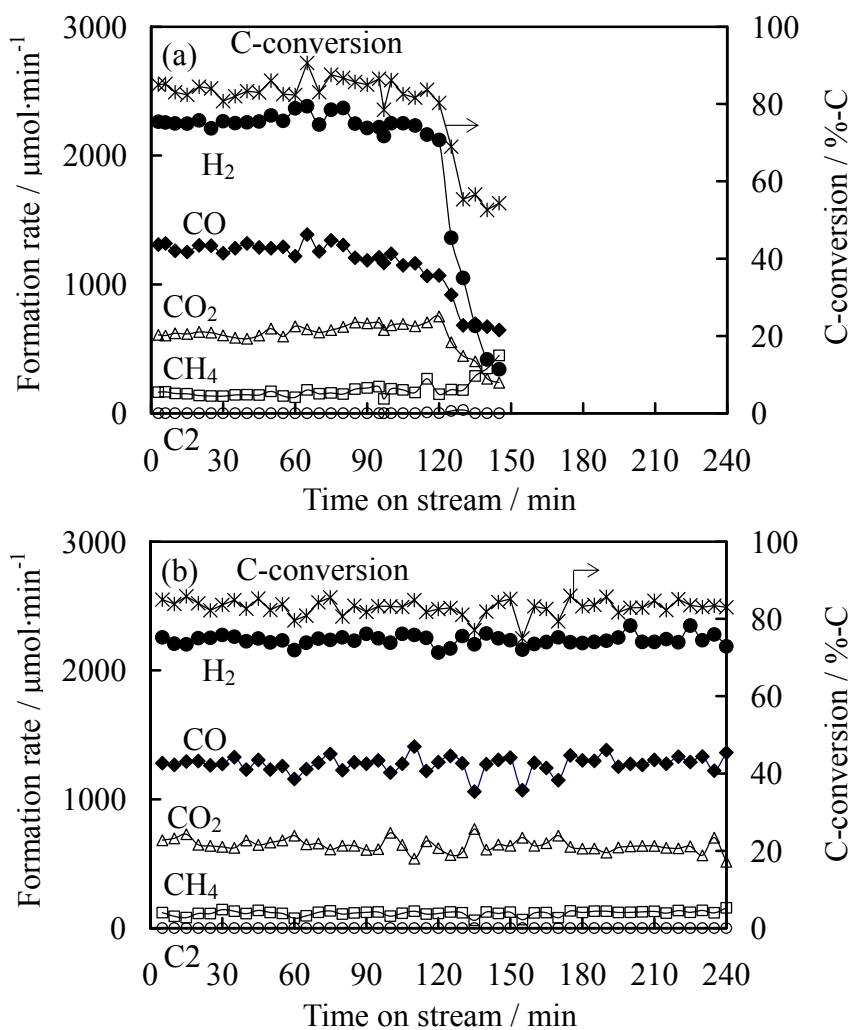


Figure 6. Catalytic performance in steam gasification of cedar wood as a function of time on stream over the catalysts at 923 K.

(a) Pt/Ni/CA (b) Pt/Ni/CMA

Conditions: biomass; 60 mg/min (H_2O 9.2 %, C 2191 $\mu\text{mol}/\text{min}$; H 3543 $\mu\text{mol}/\text{min}$; O 1475 $\mu\text{mol}/\text{min}$), N_2 flow rate; 60 ml/min, (added H_2O)/C=0.5 (steam flow rate 1110 $\mu\text{mol}/\text{min}$), H_2 reduction at 773 K, 30 min.

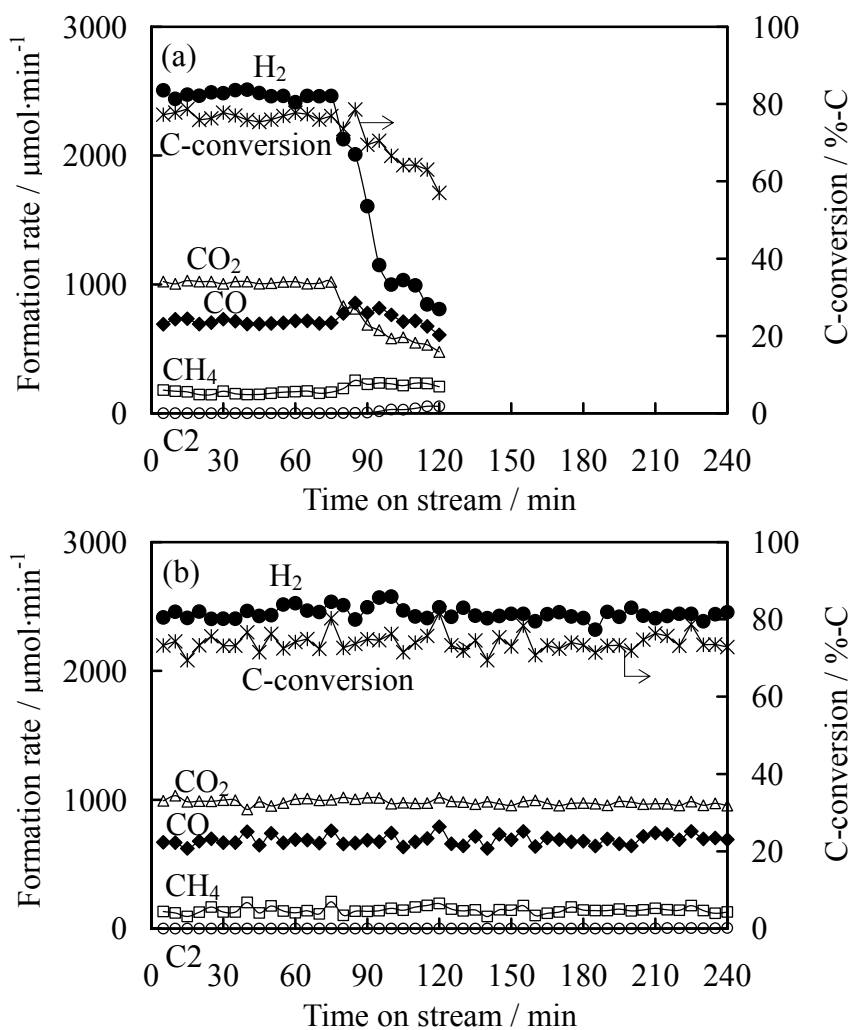


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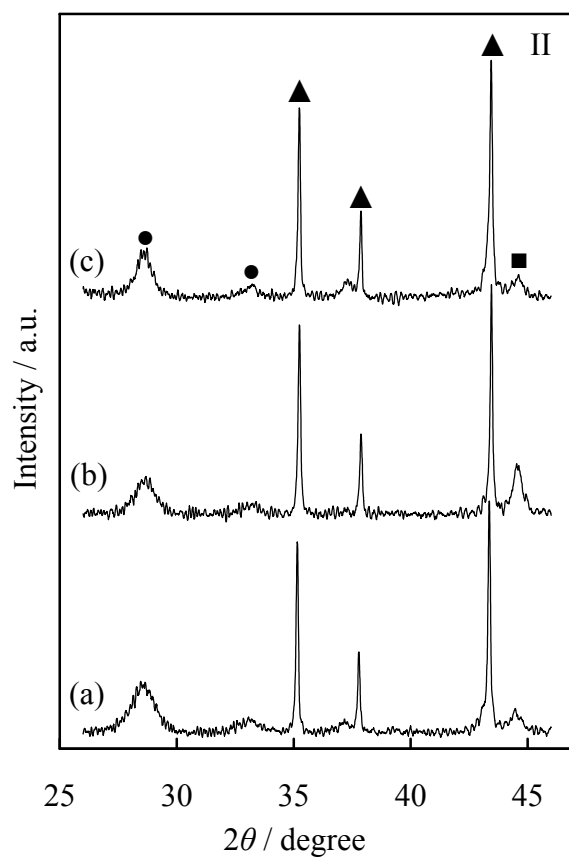
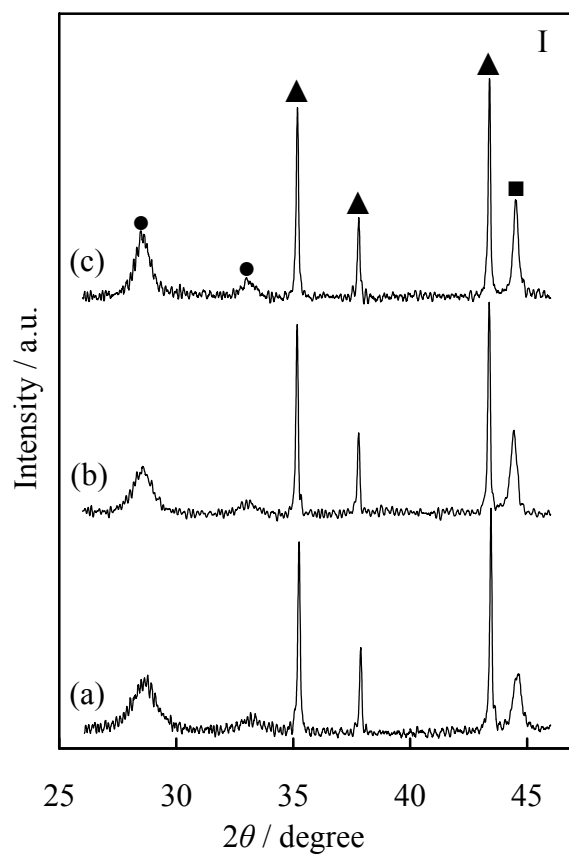


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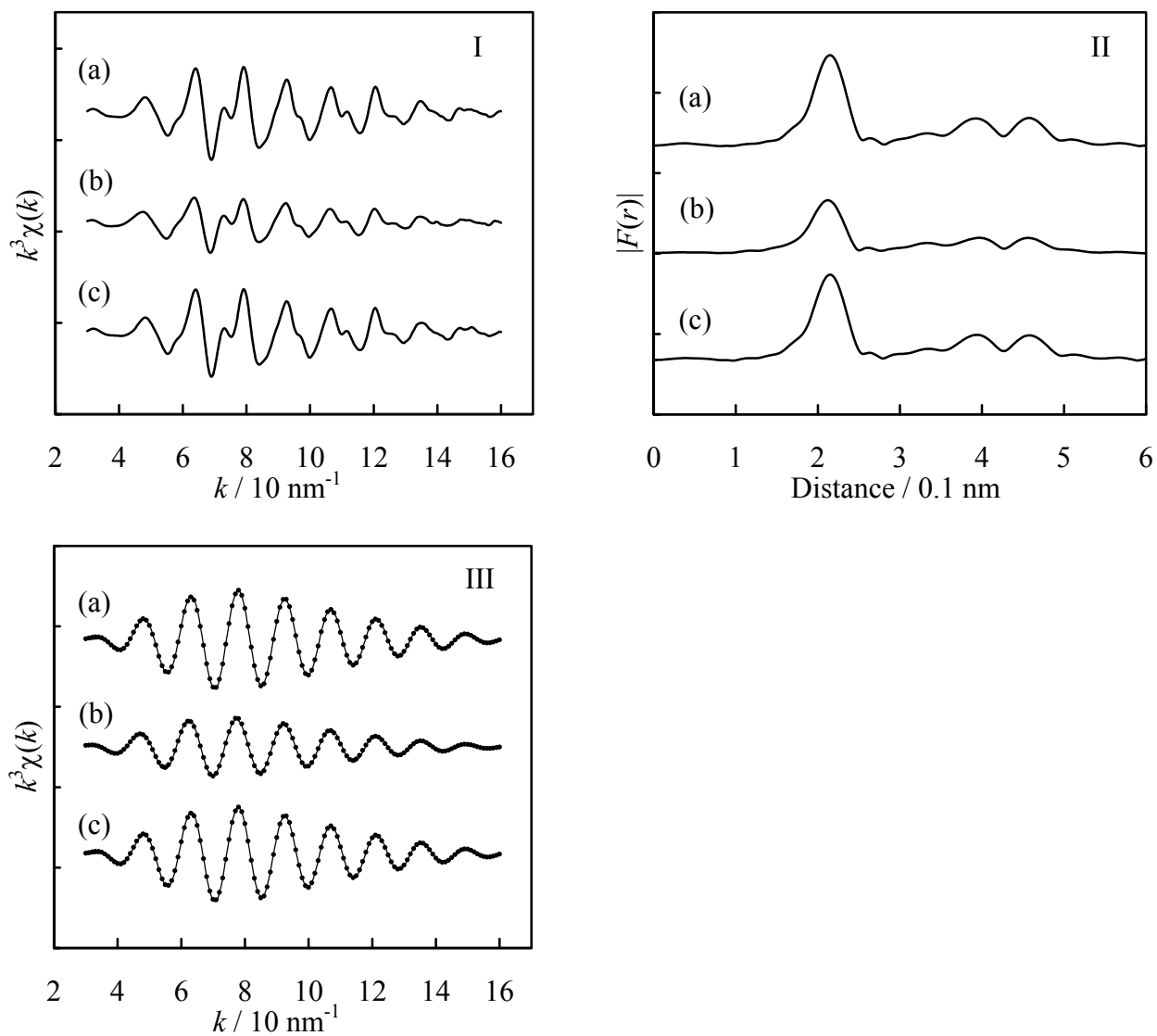


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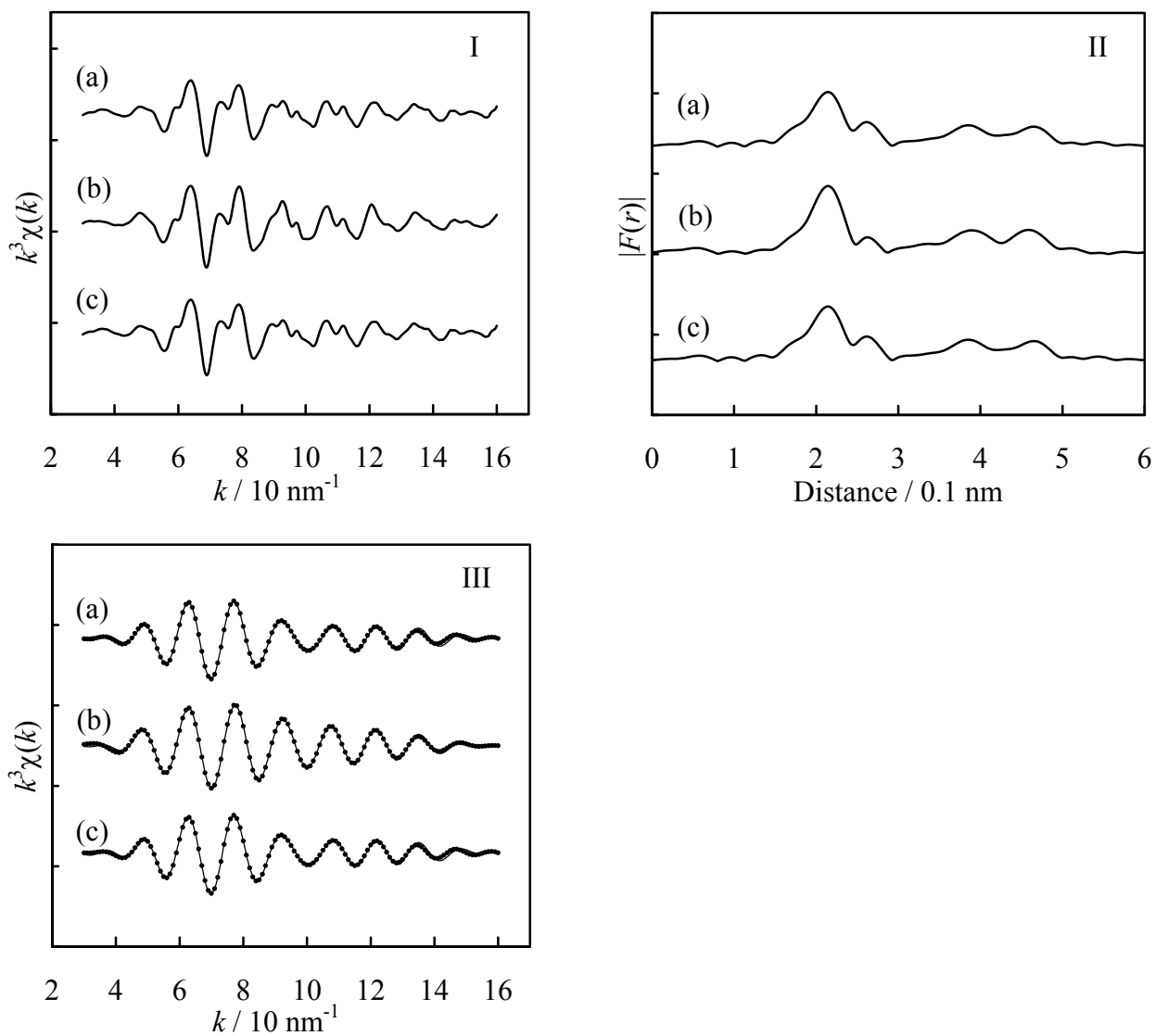


Figure 10. Results of Ni *K*-edge EXAFS analysis of Pt/Ni/CMA.

(a) After H_2 reduction, (b) after the reaction at 923 K (Figure 6), (c) after the regeneration.

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