

Supplementary Materials

Na₂WO₄/Mn/SiO₂ catalyst pellets for upgrading H₂S-containing biogas via the oxidative coupling of methane

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Table S1: Higher heating values of OCM products in STP conditions.

	HHV (MJ/Nm ³)
CH ₄	39.9
C ₂ H ₂	58.1
C ₂ H ₄	63.1
C ₂ H ₆	69.8
C ₃ H ₆	92.1
C ₃ H ₈	99.3

Table S2: Compositions of OCM products.

Catalyst	Reaction condition				Product composition (mol%)								Balance (%)		
	GHSV (h ⁻¹)	Feed (v/v/v)	Temperature (°C)		CH ₄	O ₂	N ₂	CO	CO ₂	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₈	C Sum	
N(8)M(0.5)	10,000	27:2:1	800		53.9	2.3	4.4	0.4	37.7	0.0	0.4	0.7	0.0	0.0	105.9
N(8)M(0.5)P(1.5)	20,000	27:2:1	800		53.7	2.4	4.5	0.4	37.6	0.0	0.6	0.8	0.0	0.0	105.1
N(8)M(0.5)P(1.5)	10,000	27:2:1	750		54.5	3.2	4.6	0.0	37.0	0.0	0.2	0.5	0.0	0.0	106.6
N(8)M(0.5)P(1.5)	10,000	27:2:1	800		52.2	1.6	4.9	0.8	38.2	0.0	1.2	1.1	0.1	0.0	105.9
N(8)M(0.5)P(1.5)	10,000	81:6:3	800		51.5	1.0	4.7	0.9	39.4	0.01	1.4	1.0	0.10	0.01	106.3
N(8)M(0.5)P(1.5)	10,000	135:10:5	800		50.7	0.0	4.5	1.2	40.3	0.0	2.0	1.1	0.2	0.0	107.7
N(8)M(0.5)P(1.5)	10,000	27:2:1	850		50.8	0.0	5.1	1.1	39.7	0.1	2.1	1.0	0.2	0.0	105.7
N(8)M(0.5)P(1.5)	10,000	25:4:1	800		48.2	1.9	5.2	1.1	39.5	0.0	2.6	1.3	0.2	0.0	102.0
N(8)M(0.5)P(1.5)	10,000	23:6:1	800		43.4	1.9	6.2	1.5	42.0	0.0	3.5	1.1	0.2	0.0	99.2
N(8)M(0.5)P(1.5)	10,000	21:8:1	800		35.5	1.3	7.5	2.5	47.0	0.1	4.9	1.0	0.2	0.0	102.4
N(8)M(0.5)P(1.5)	5,000	27:2:1	800		50.8	0.7	4.7	0.9	39.7	0.0	1.7	1.2	0.1	0.0	108.6
N(8)M(0.5)P(1.5)	3,333	27:2:1	800		50.2	0.0	5.2	1.0	40.1	0.0	2.0	1.3	0.1	0.0	104.4
N(8)M(0.5)P(1.5)	2,000	27:2:1	800		50.4	0.0	5.0	1.1	40.1	0.0	2.4	0.9	0.1	0.0	101.3
N(8)M(0.5)P(1.5)	1,000	27:2:1	800		50.2	0.0	5.1	1.4	39.9	0.0	2.5	0.7	0.1	0.0	108.0
N(8)V(0.5)P(1.5)	10,000	27:2:1	800		52.1	1.2	4.9	0.7	38.7	0.0	1.1	1.1	0.1	0.0	103.2
N(8)S(0.5)P(1.5)	10,000	27:2:1	800		52.3	1.4	4.9	0.6	38.5	0.0	1.0	1.1	0.1	0.0	107.4
N(8)P(1.5)	10,000	27:2:1	800		54.0	2.6	4.7	0.3	37.3	0.0	0.4	0.6	0.0	0.0	110.5
N(8)M(0.25)P(1.5)	10,000	27:2:1	800		52.4	0.9	5.0	0.9	38.4	0.0	1.2	1.1	0.1	0.0	110.4
N(8)M(1)P(1.5)	10,000	27:2:1	800		51.9	1.6	4.8	0.7	38.5	0.0	1.3	1.1	0.1	0.0	108.0

N(8)M(2)P(1.5)	10,000	27:2:1	800	52.0	1.8	4.8	0.7	38.4	0.0	1.1	1.1	0.1	0.0	107.3
N(8)M(0.5)P(0.75)	10,000	27:2:1	800	52.1	1.5	5.2	0.7	38.3	0.0	1.1	1.0	0.1	0.0	107.4
N(8)M(0.5)P(3)	10,000	27:2:1	800	51.8	1.1	5.0	0.9	38.7	0.0	1.3	1.2	0.1	0.0	103.6
N(8)M(0.5)P(6)	10,000	27:2:1	800	51.6	0.3	5.0	1.0	39.3	0.0	1.4	1.2	0.1	0.0	104.2
N(8)M(0.5)A(1.5)	10,000	27:2:1	800	54.4	2.6	4.6	0.6	37.34	0.00	0.2	0.3	0.01	0.00	100.4
N(8)M(0.5)Mo(1.5)	10,000	27:2:1	800	54.4	2.9	4.3	0.6	37.3	0.0	0.2	0.4	0.0	0.0	109.5
N(8)M(0.5)Mg(1.5)	10,000	27:2:1	800	53.6	2.2	4.5	0.7	38.40	0.00	0.2	0.4	0.01	0.00	106.9
N(8)M(0.5)Mn(1.5)	10,000	27:2:1	800	52.9	2.1	4.8	0.7	37.80	0.00	0.8	0.9	0.04	0.00	104.8

Table S3: OCM results at 800 °C using catalyst pellets depending on organic binders.^a

Catalyst	Methane conversion (%)	C ₂₊ selectivity (%) ^b	Olefin selectivity (%) ^c	C ₂₊ yield (%) ^b	Olefin/Paraffin (mol/mol) ^d	O ₂ conversion (%)	HHV (MJ/Nm ³) ^e
N(8)M(0.5)P(1.5)	10.0	83.9	44.4	8.39	1.12	77.8	41.0
N(8)V(0.5)P(1.5)	9.67	78.0	38.8	7.55	0.99	84.8	41.0
N(8)S(0.5)P(1.5)	9.92	77.6	39.5	7.70	1.03	81.6	40.9

^a Reaction conditions: GHSV=10,000 h⁻¹, 0.18 mL of catalyst, 800 °C, 30 mL/min of flow rate composed of CH₄/O₂/N₂/CO₂/H₂S = 16.1/2/1/10.7/0.1 (v/v/v/v).

^b C₂₊ indicates paraffins and olefins including ethane, ethylene, propane, propylene, and other higher carbon number hydrocarbons.

^c Olefin contains ethylene and propylene.

^d Paraffin contains ethane and propane.

^e 0 °C, 1 atm.

Table S4: OCM results at 800 °C using inorganic binders.^a

Catalyst	Methane conversion (%)	C ₂₊ selectivity (%) ^b	Olefin selectivity (%) ^c	C ₂₊ yield (%) ^b	Olefin/Paraffin (mol/mol) ^d	O ₂ conversion (%)
P25	11.1	6.00	2.99	0.67	0.99	100.0
Al ₂ O ₃	11.3	10.3	4.66	1.16	0.82	100.0
Mont	8.53	7.99	3.08	0.68	0.63	100.0
MgO	3.32	56.3	23.7	1.87	0.73	55.0
Mn ₂ O ₃	7.99	11.9	3.57	0.95	0.43	100.0

^a Reaction conditions: GHSV=10,000 h⁻¹ 0.18 mL of catalyst, 800 °C, 30 mL/min of flow rate with CH₄: O₂: N₂: CO₂: H₂S=16.1: 2: 1: 10.7: 0.1 (v/v/v/v).

^b C₂₊ contains all coupled products including ethane, ethylene, propane, propylene, and other higher carbon number hydrocarbons.

^c Olefin contains ethylene and propylene.

^d Paraffin contains ethane and propane

Table S5: OCM results at 800 °C using catalyst pellets depending on inorganic binders with different feed composition.^a

Catalyst	Methane conversion (%)	C ₂₊ selectivity (%) ^b	Olefin selectivity (%) ^c	C ₂₊ yield (%) ^b	Olefin/Paraffin (mol/mol) ^d	O ₂ conversion (%)
CH ₄ /O ₂ /N ₂ = 16.2/2/11.8 (v/v/v)						
N(8)M(0.5)	14.8	74.7	42.2	11.1	1.30	100.0
N(8)M(0.5)P(1.5)	18.9	72.7	43.5	13.7	1.49	100.0
N(8)M(0.5)A(1.5)	4.32	40.1	13.5	1.73	0.50	66.2
N(8)M(0.5)Mo(1.5)	13.0	72.5	38.5	9.46	1.13	82.9
N(8)M(0.5)Mg(1.5)	7.66	32.0	12.3	2.45	0.63	86.8
N(8)M(0.5)Mn(1.5)	16.5	80.8	45.9	13.3	1.31	100.0
CH ₄ /O ₂ /N ₂ /CO ₂ = 16.2/2/1/10.8 (v/v/v/v)						
N(8)M(0.5)	13.3	81.3	45.3	10.8	1.26	100.0
N(8)M(0.5)P(1.5)	14.9	88.6	52.9	13.2	1.48	100.0
N(8)M(0.5)A(1.5)	3.91	45.7	16.4	1.79	0.56	63.5
N(8)M(0.5)Mo(1.5)	11.1	85.0	46.1	9.43	1.19	80.4
N(8)M(0.5)Mg(1.5)	6.50	42.5	16.8	2.76	0.66	86.5
N(8)M(0.5)Mn(1.5)	13.9	93.3	52.7	12.9	1.30	93.9
CH ₄ /O ₂ /N ₂ /CO ₂ /H ₂ S = 16.2/2/1/10.7/0.1 (v/v/v/v/v)						
N(8)M(0.5)	7.85	51.0	21.0	3.99	0.70	65.4
N(8)M(0.5)P(1.5)	10.0	83.9	44.4	8.39	1.12	77.8
N(8)M(0.5)A(1.5)	3.43	49.0	16.7	1.68	0.52	59.2
N(8)M(0.5)Mo(1.5)	6.00	33.3	11.0	1.95	0.50	56.6
N(8)M(0.5)Mg(1.5)	7.76	28.9	10.5	2.19	0.58	65.9
N(8)M(0.5)Mn(1.5)	8.63	71.7	34.9	6.19	0.95	70.6

^a Reaction conditions: GHSV=10,000 h⁻¹ 0.18 mL of catalyst, 800 °C, 30 mL/min of flow rate.

^b C₂₊ contains all coupled products including ethane, ethylene, propane, propylene, and other higher carbon number hydrocarbons.

^c Olefin contains ethylene and propylene.

^d Paraffin contains ethane and propane

Table S6: Preparation of catalyst pellets.

Nomenclature of the pellet	Binders used		Amount of each components (g)		
	Organic (OB)	Inorganic (IB)	NWM	OB	IB
N(8)M(0.5)	MC	-	8	0.5	0
N(8)M(0.5)P(1.5)	MC	P25	8	0.5	1.5
N(8)M(0.5)A(1.5)	MC	Al ₂ O ₃	8	0.5	1.5
N(8)M(0.5)Mo(1.5)	MC	Mont	8	0.5	1.5
N(8)M(0.5)Mg(1.5)	MC	MgO	8	0.5	1.5
N(8)M(0.5)Mn(1.5)	MC	Mn ₂ O ₃	8	0.5	1.5
N(8)V(0.5)P(1.5)	PVA	P25	8	0.5	1.5
N(8)S(0.5)P(1.5)	Starch	P25	8	0.5	1.5
N(8)P(1.5)	MC	P25	8	0	1.5
N(8)M(0.25)P(1.5)	MC	P25	8	0.25	1.5
N(8)M(0.5)P(1.5)	MC	P25	8	0.5	1.5
N(8)M(1)P(1.5)	MC	P25	8	1	1.5
N(8)M(2)P(1.5)	MC	P25	8	2	1.5
N(8)M(0.5)	MC	P25	8	0.5	0
N(8)M(0.5)P(0.75)	MC	P25	8	0.5	0.75
N(8)M(0.5)P(3)	MC	P25	8	0.5	3
N(8)M(0.5)P(6)	MC	P25	8	0.5	6

Table S7: Higher heating values of products at STP conditions.

Compound	HHV (MJ/Nm ³)
CH ₄	39.9
C ₂ H ₂	58.1
C ₂ H ₄	63.1
C ₂ H ₆	69.8
C ₃ H ₆	92.1
C ₃ H ₈	99.3

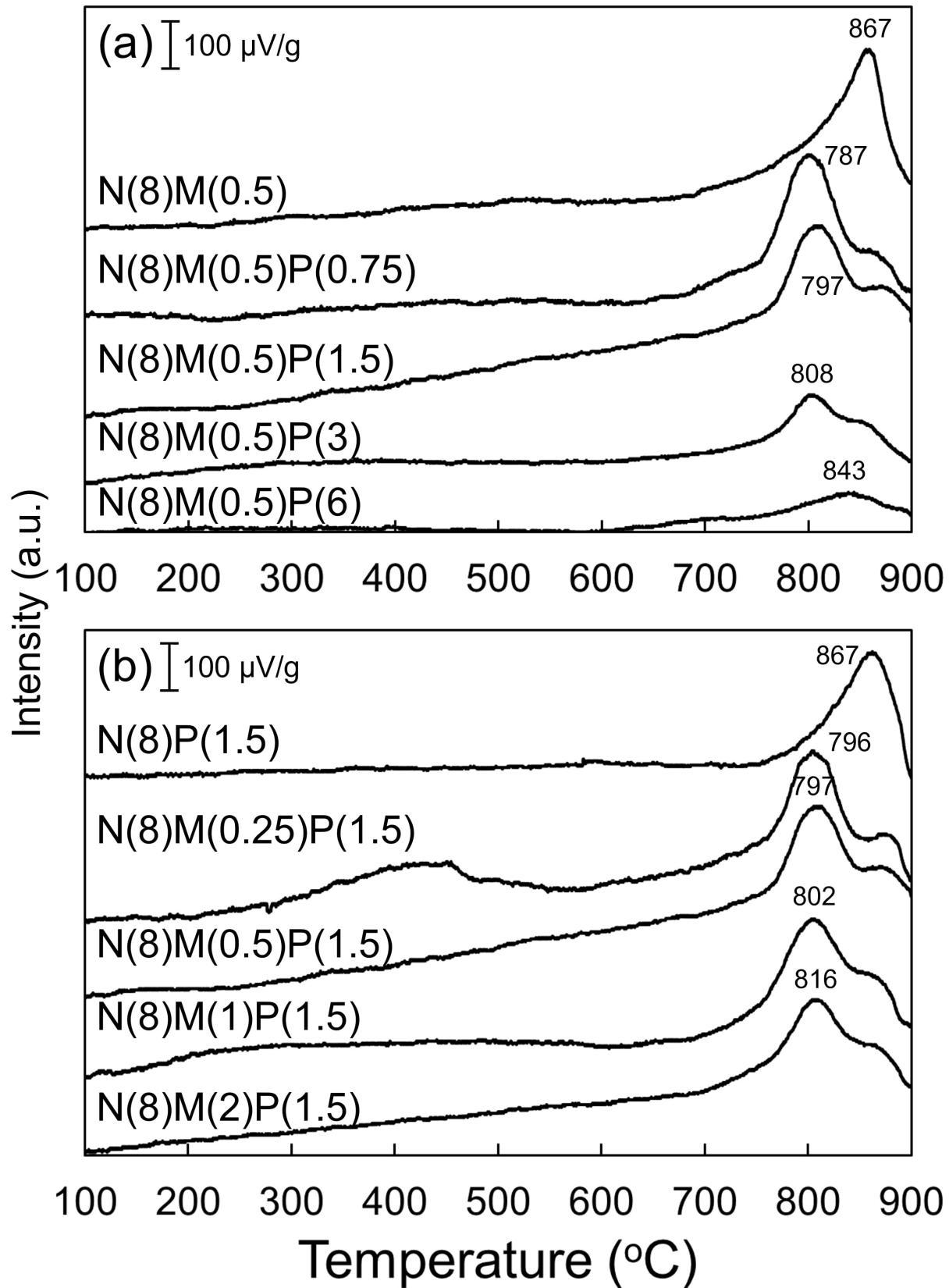


Figure S1: O₂ TPD results of fresh catalyst pellets depending on the fractions of (a) inorganic binder P25 and (b) organic binder MC.

■: α -cristobalite ▼: MnWO_4 ●: Na_2WO_4
 ▲: $\text{Mn}_7\text{SiO}_{12}$ ★: Quartz ◆: Rutile

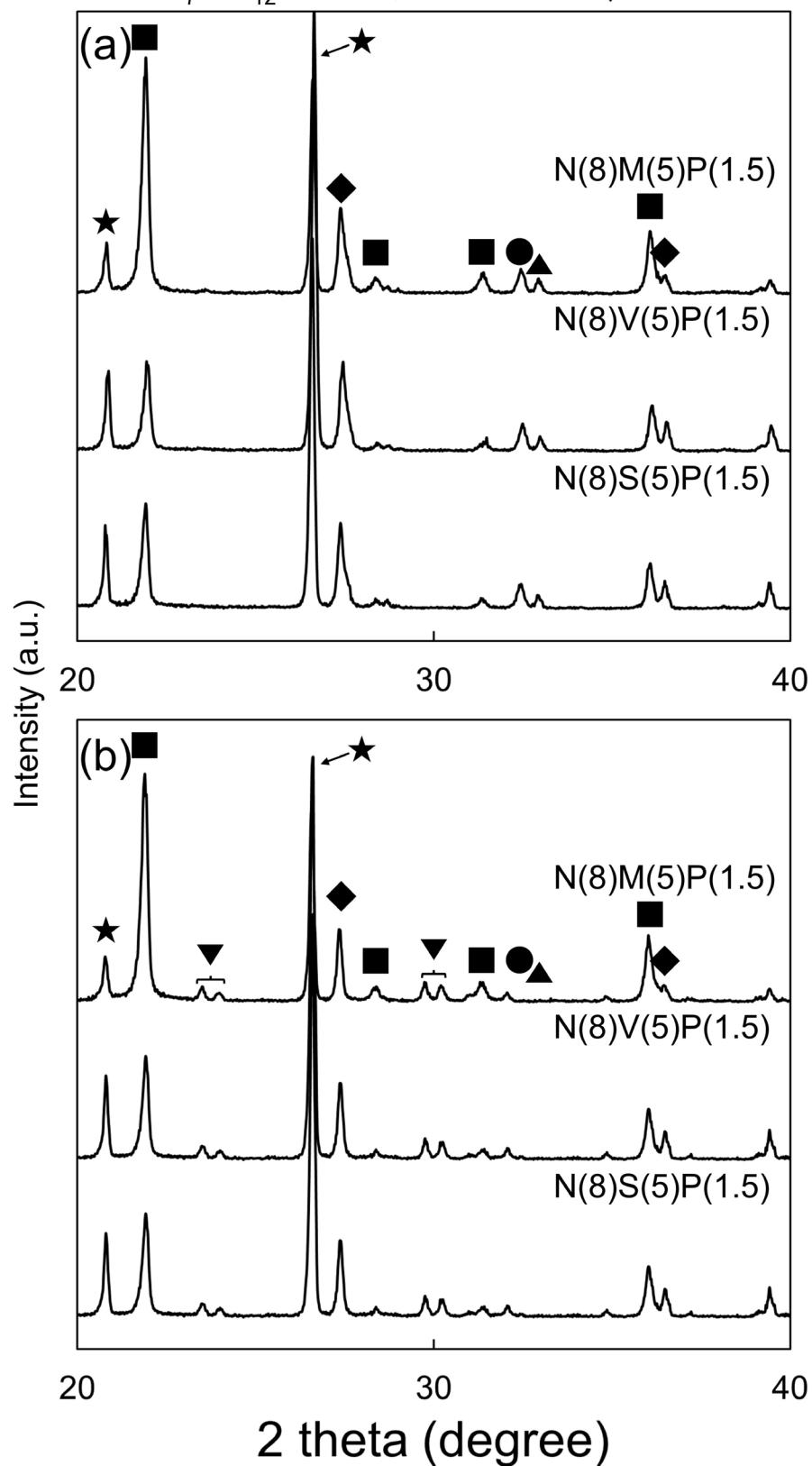


Figure S2: Powder XRD results of (a) fresh and (b) spent catalyst pellets depending on organic binders.

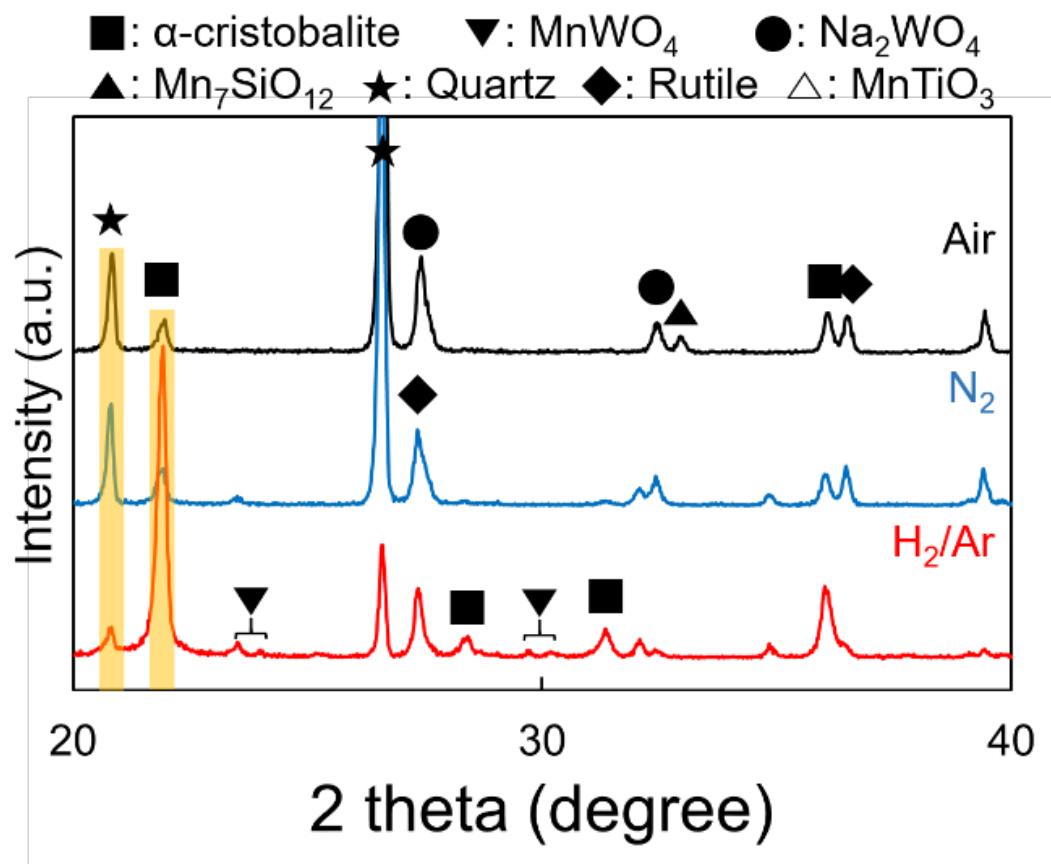


Figure S3: Powder XRD results of fresh N(8)M(0.5)P(1.5) depending on the calcination environments of air, N₂, and 5% H₂/Ar.

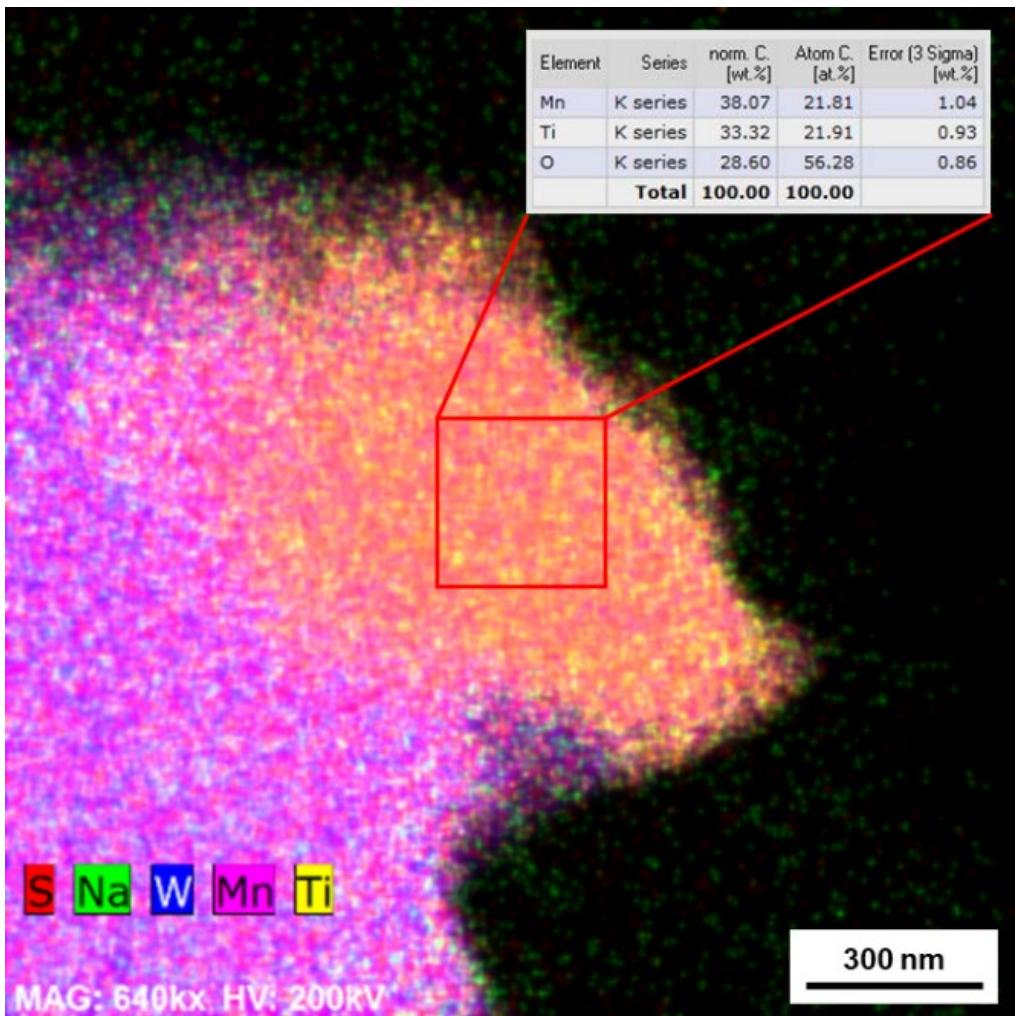


Figure S4: TEM-EDS result of spent N(8)M(0.5)P(1.5).

■: α -cristobalite ▼: MnWO_4 ●: Na_2WO_4
 ▲: $\text{Mn}_7\text{SiO}_{12}$ ★: Quartz ◆: Rutile △: MnTiO_3

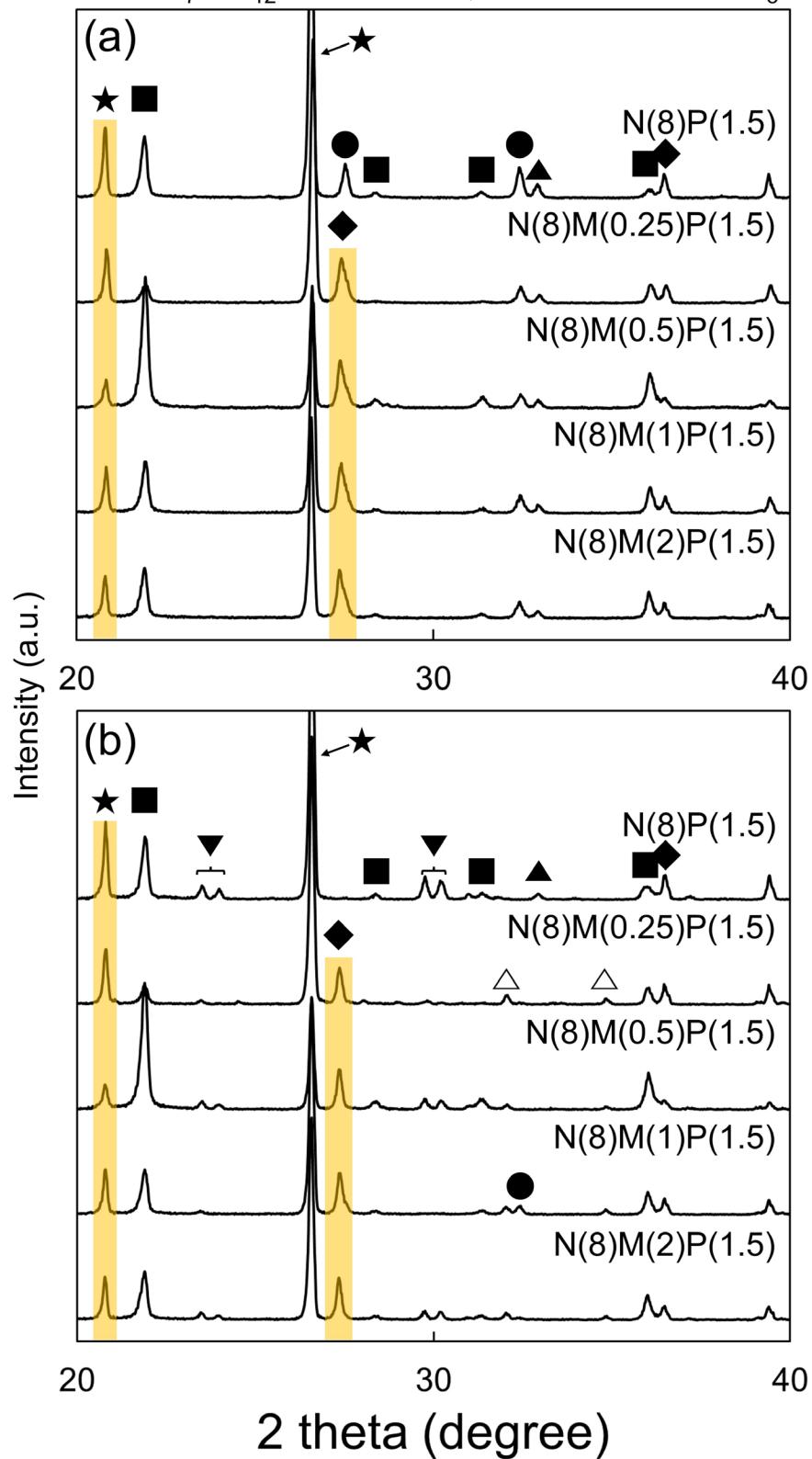


Figure S5: Powder XRD results of (a) fresh and (b) spent catalyst pellets depending on the amount of inorganic binder P25.

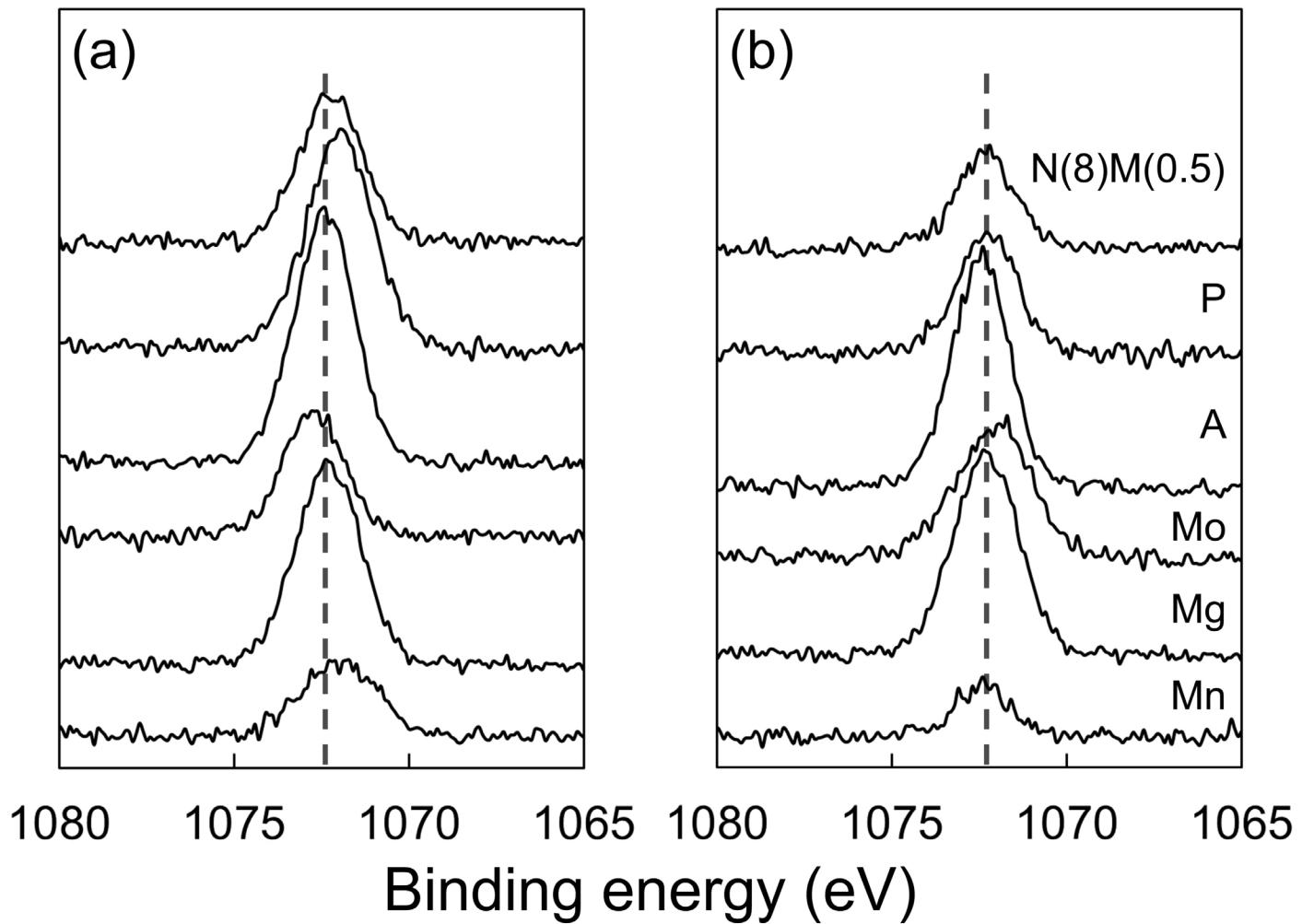


Figure S6: Na 1s XPS results of (a) fresh and (b) spent catalyst pellets depending on inorganic binders.

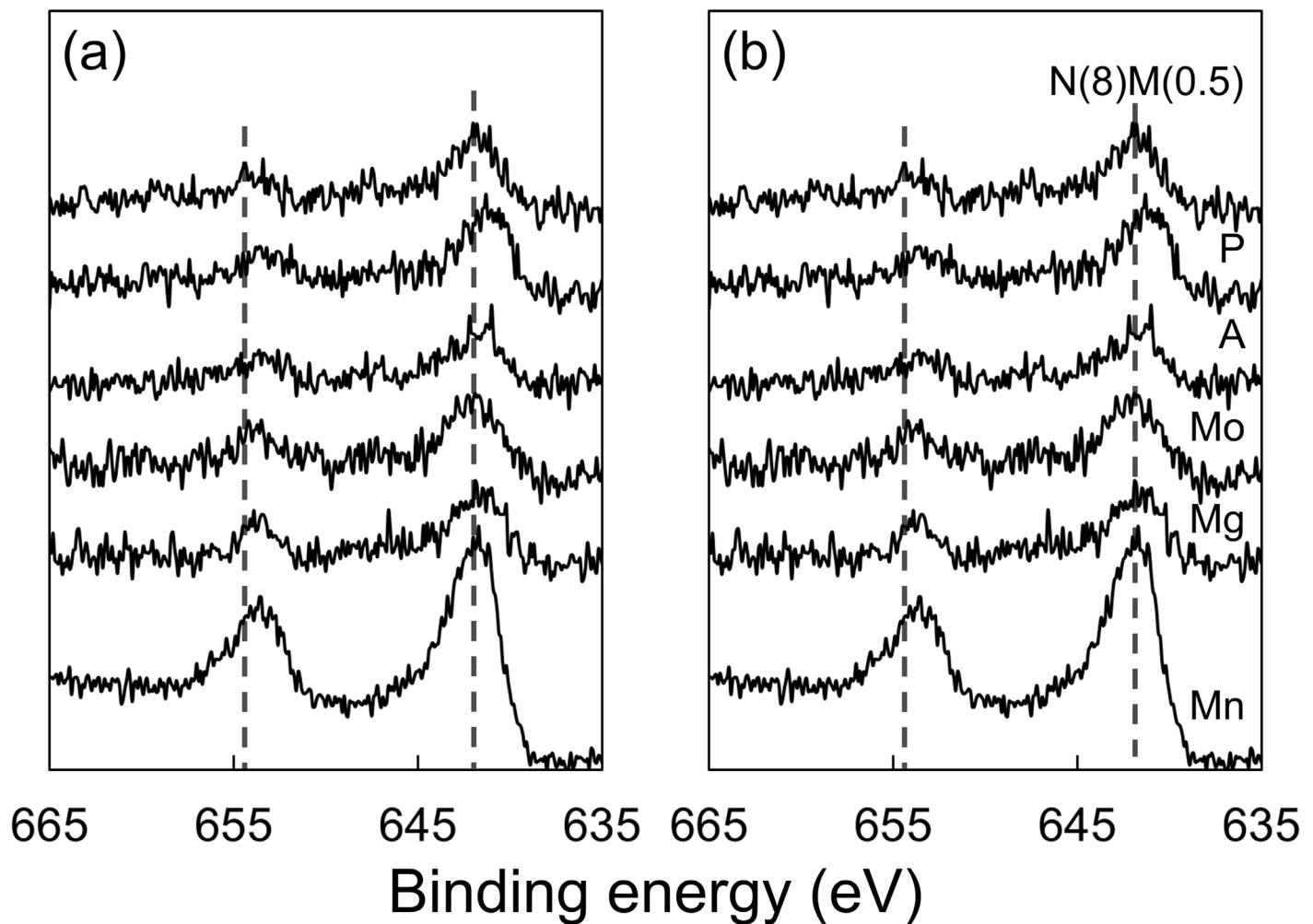


Figure S7: Mn 2p XPS results of (a) fresh and (b) spent catalyst pellets depending on inorganic binders.

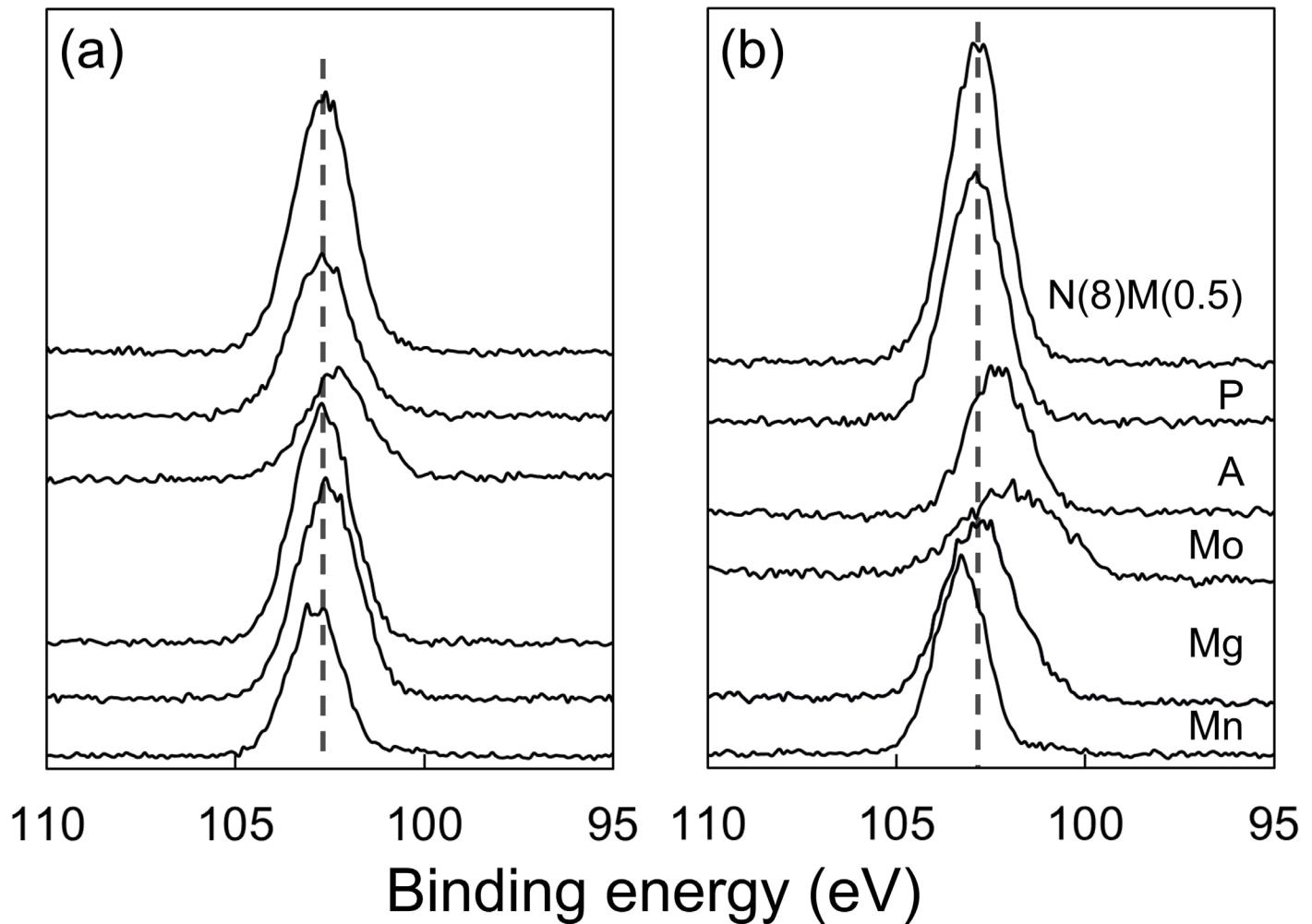


Figure S8: Si 2p XPS results of (a) fresh and (b) spent catalyst pellets depending on inorganic binders.

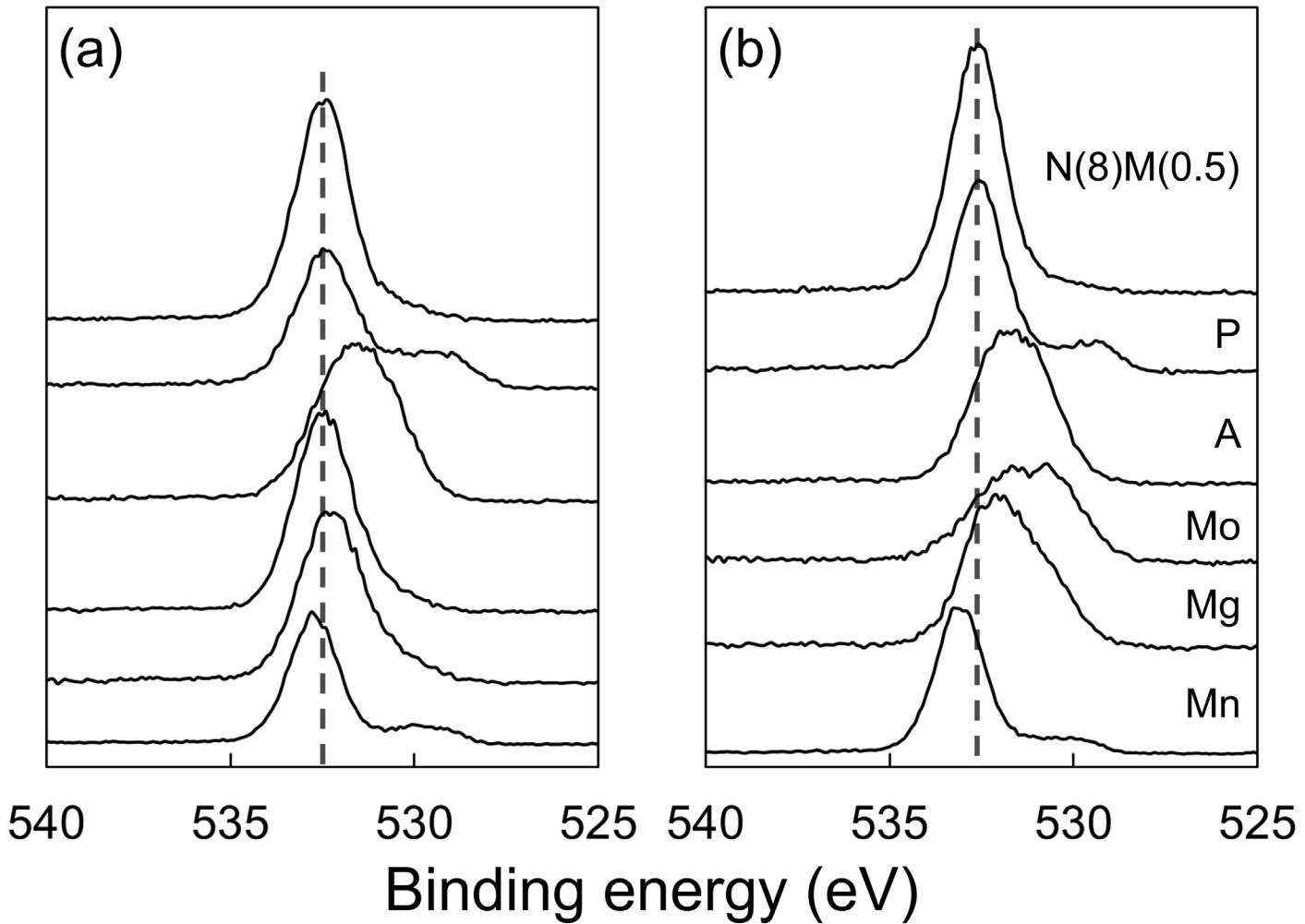


Figure S9: O 1s XPS results of (a) fresh and (b) spent catalyst pellets depending on inorganic binders.

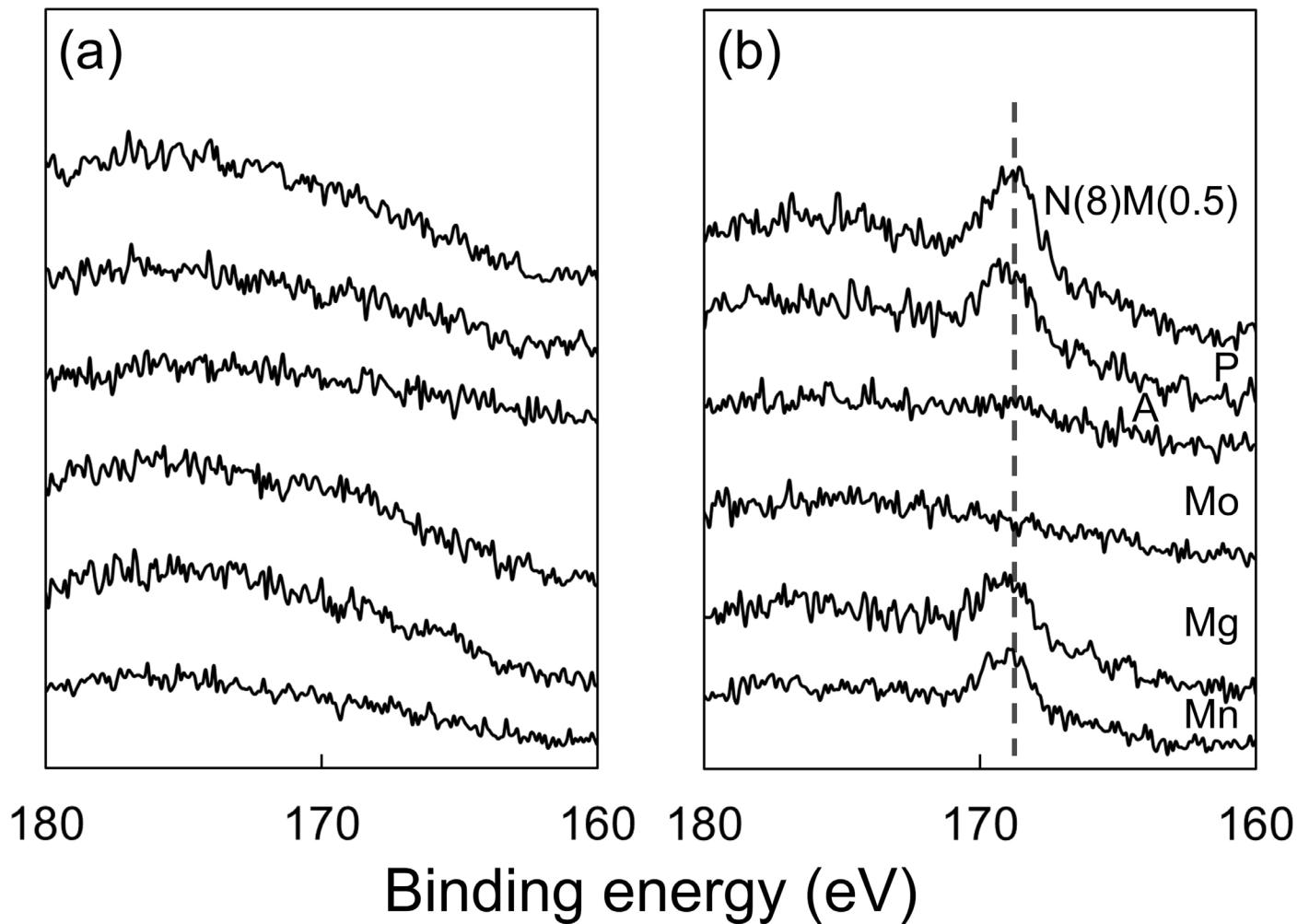


Figure S10: S 2p XPS results of (a) fresh and (b) spent catalyst pellets depending on inorganic binders.

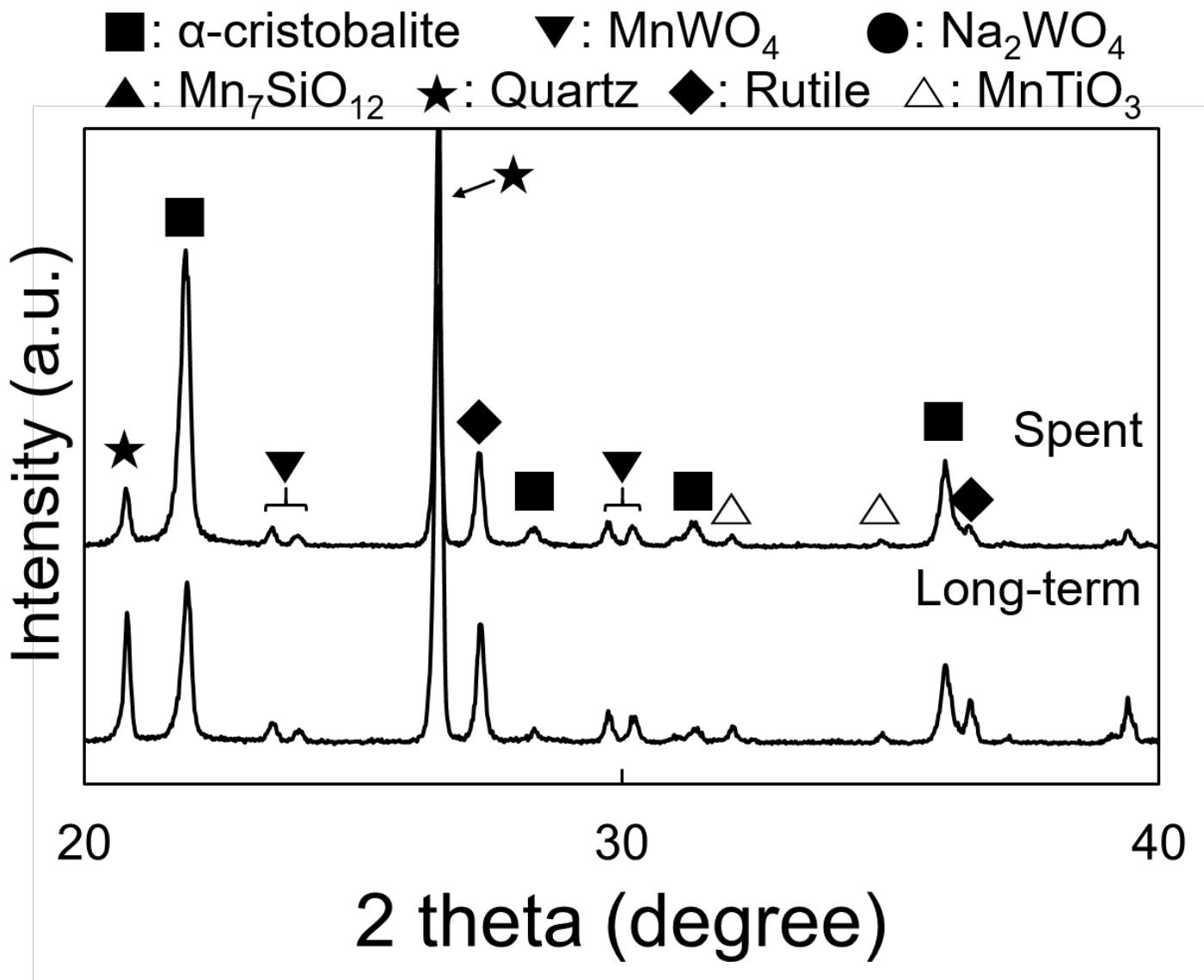


Figure S11: Powder XRD results of spent catalysts after 100 h reaction.