

ARTICLE

Electronic Supplementary Information

**Molten Salt Synthesis of CrMnFeNi Alloy Nanopowder Passivated by TiO_x-ZrO_y Shell
Used as a Superior Catalyst Support in Liquid-phase Hydrogenation**

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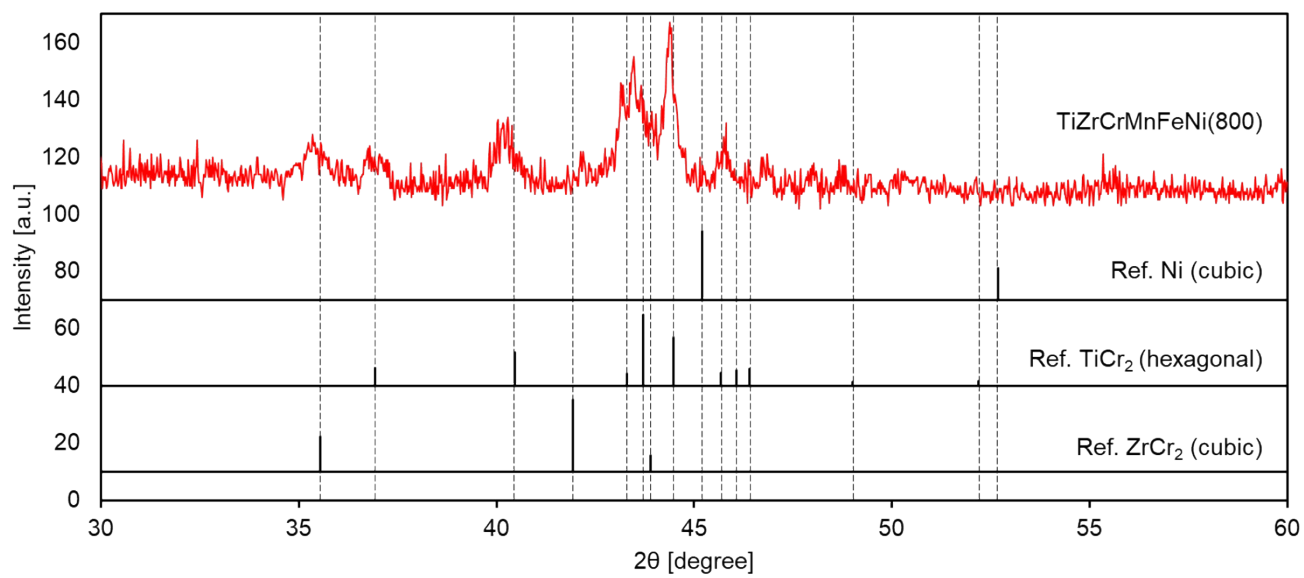


Fig. S1 XRD patterns for TiZrCrMnFeNi(800).

Table S1 Space group and crystal system for Laves phase intermetallic compounds.

Intermetallic compound	Space group	Crystal system
TiCr ₂	P63/mmc	hexagonal
TiMn ₂	P63/mmc	hexagonal
TiFe ₂	P63/mmc	hexagonal
TiNi ₂	n.d.	n.d.
ZrCr ₂	Fd3(-)m	cubic
ZrMn ₂	Fd3(-)m	cubic
ZrFe ₂	P63/mmc	hexagonal
ZrNi ₂	Fd3(-)m	cubic

Table S2 Elemental weight ratios measured using XPS, SEM–EDX, and TEM–EDX.

Sample	Elemental weight ratio [wt%]									
	Method	Position	Ti	Zr	Cr	Mn	Fe	Ni	O	Average
TiZrCrMnFeNi(Pre)	XPS	#1	5.1	19.5	11.2	11.5	8.4	8.2	36.1	Ti/Zr/Cr/Mn/Fe/Ni/O =6.8/18.7/10.1/12.2/9.7/7.6/35.0
		#2	5.3	18.6	8.4	11.9	12.7	8.6	34.4	
		#3	10.1	17.8	10.7	13.1	7.9	5.9	34.4	
TiZrCrMnFeNi(800)	XPS	#1	13.3	35.7	3.6	3.6	3.1	3.0	37.6	Ti/Zr/Cr/Mn/Fe/Ni/O =12.7/33.5/5.3/4.1/3.9/2.3/38.1
		#2	14.0	34.2	8.0	3.1	4.1	0	37	
		#3	10.9	30.5	4.4	5.6	4.6	3.9	40.2	
	SEM-EDX	Overall	8.3	47.9	7.5	7.2	7.9	7.8	13.3	Ti/Zr/Cr/Mn/Fe/Ni/O =8.2/48.4/8.0/8.0/8.7/9.2/9.5
		#1	6.9	71.7	3.2	3.0	3.4	3.3	8.6	
		#2	9.8	41.1	10.0	9.1	10.2	10.6	9.2	
	TEM-EDX	#3	7.8	32.8	11.5	12.6	13.5	14.9	6.8	Ti/Zr/Cr/Mn/Fe/Ni/O =13.8/40.2/12.8/9.0/9.1/10.9/4.2
		#1	9.0	12.1	59.9	7.3	10.3	1.5	0.0	
		#2	1.5	1.5	13.8	26.3	27.6	28.9	0.4	
		#3	53.6	16.9	24.1	1.7	3.1	0.6	0.0	
		#4	3.2	4.0	11.7	26.0	26.3	28.0	0.8	
		#5	28.3	33.7	25.8	3.2	5.8	1.6	1.7	
		#6	4.0	7.7	66.7	8.4	11.8	1.4	0.0	
		#7	1.9	5.8	7.0	29.5	19.8	31.7	4.3	
		#8	3.4	10.2	18.7	20.0	25.8	17.1	4.9	
		#9	3.7	10.0	8.5	24.8	20.0	26.0	7.1	
		#10	5.8	92.6	0.1	0.1	0.3	0.4	0.7	
		#11	17.6	27.6	3.6	15.1	15.4	17.0	3.7	
		#12	76.9	19.7	0.3	0.4	0.5	0.5	1.7	
		#13	5.6	88.2	0.2	0.2	0.4	0.2	5.3	
		#14	4.8	47.0	0.5	2.3	3.0	35.3	7.2	
		#15	10.5	31.3	8.9	13.7	14.4	16.6	4.5	
		#16	29.4	46.9	0.6	1.1	1.7	2.3	17.9	
		#17	2.4	42.4	44.2	6.7	3.3	1.0	0.0	
		#18	12.9	28.4	8.1	16.3	16.9	14.3	3.2	
		#19	16.6	76.7	0.2	0.2	0.4	0.1	5.7	
#20		4.8	46.6	0.5	2.4	3.2	36.4	6.1		
#21		8.8	33.2	22.9	13.7	12.4	9.0	0.0		
#22		11.6	80.9	0.1	0.4	0.4	0	7		
#23	6.5	85.8	0.2	0.1	0.3	0.3	6.9			
#24	9.6	42.8	5.1	12.9	13.4	12.9	3.2			
#25	13.8	76.7	0.2	0.3	0.5	0.1	8.4			
#26	13.2	76.9	0.3	0.3	0.6	0.2	8.5			

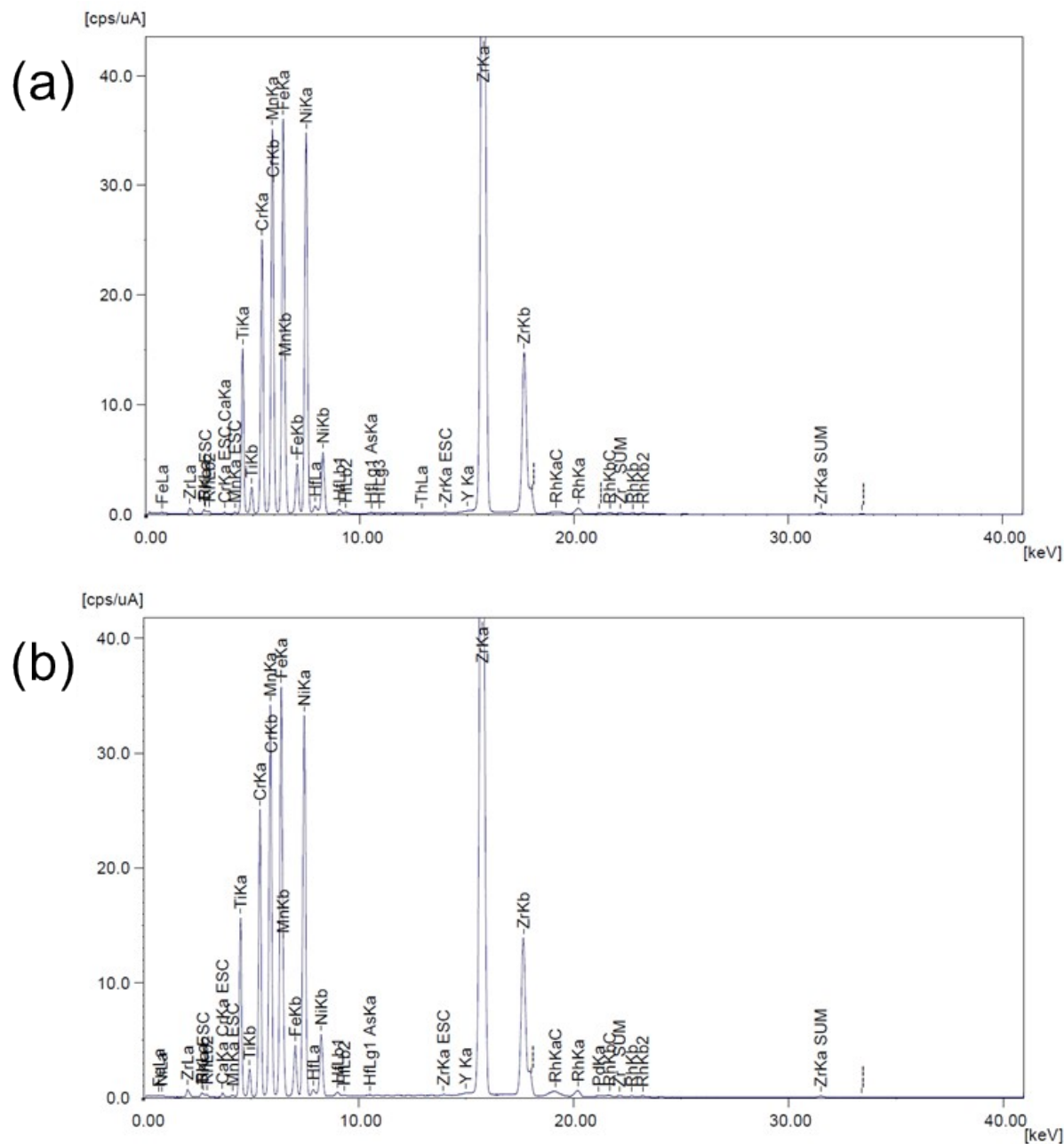


Fig. S2 EDX spectrum measured by EDX-8000 for TiZrCrMnFeNi(Pre) and TiZrCrMnFeNi(800). Molar ratios of Ti/Zr/Cr/Mn/Fe/Ni are summarized in Table 1.

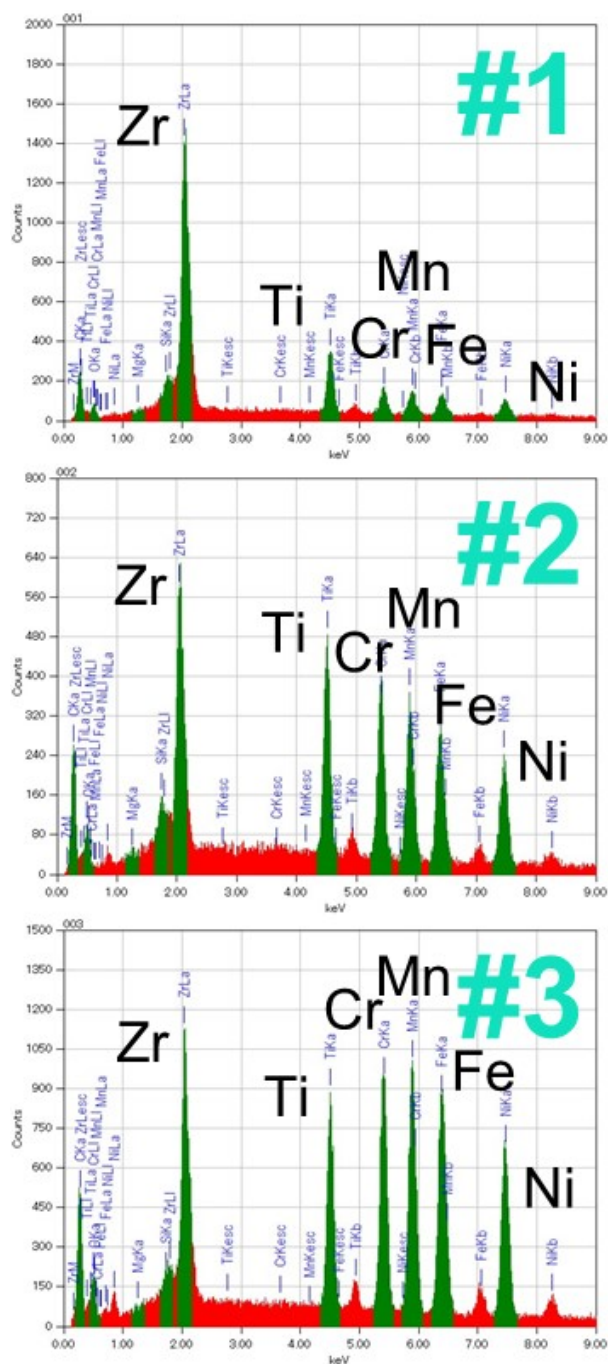


Fig. S3 EDX spectra for position #1–#3 corresponding to a SEM image of TiZrCrMnFeNi(800) in Fig. 2.

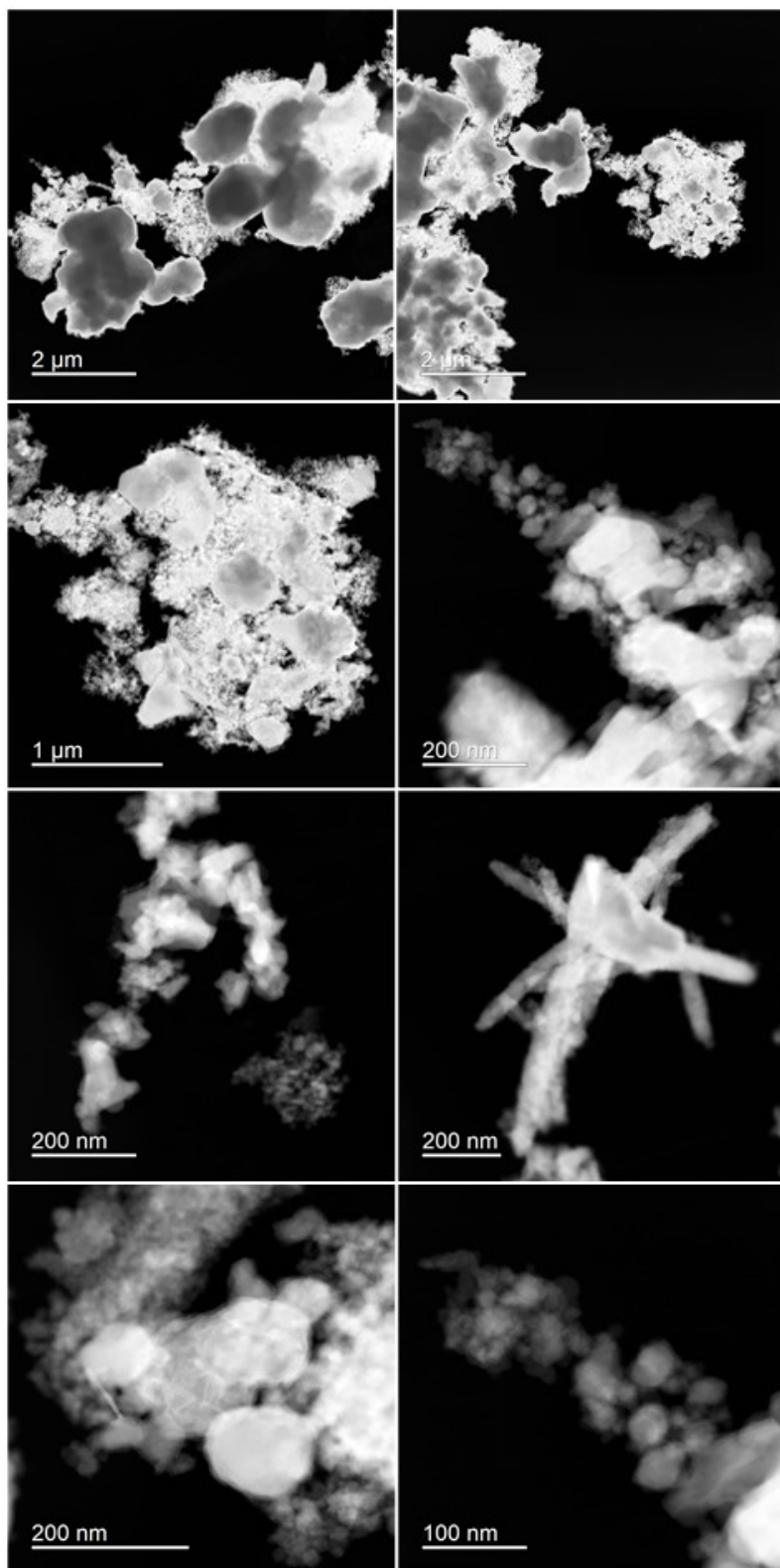


Fig. S4 TEM images for TiZrCrMnFeNi(800).

Table S3 Oxygen contents in TiZrCrMnFeNi(800) analyzed by LECO TCH-600.

Sample	No.	Used weight [mg]	Oxygen content [wt%]
TiZrCrMnFeNi(800)	1	10.7	4.38
	2	10.7	4.41
	3	10.1	4.42

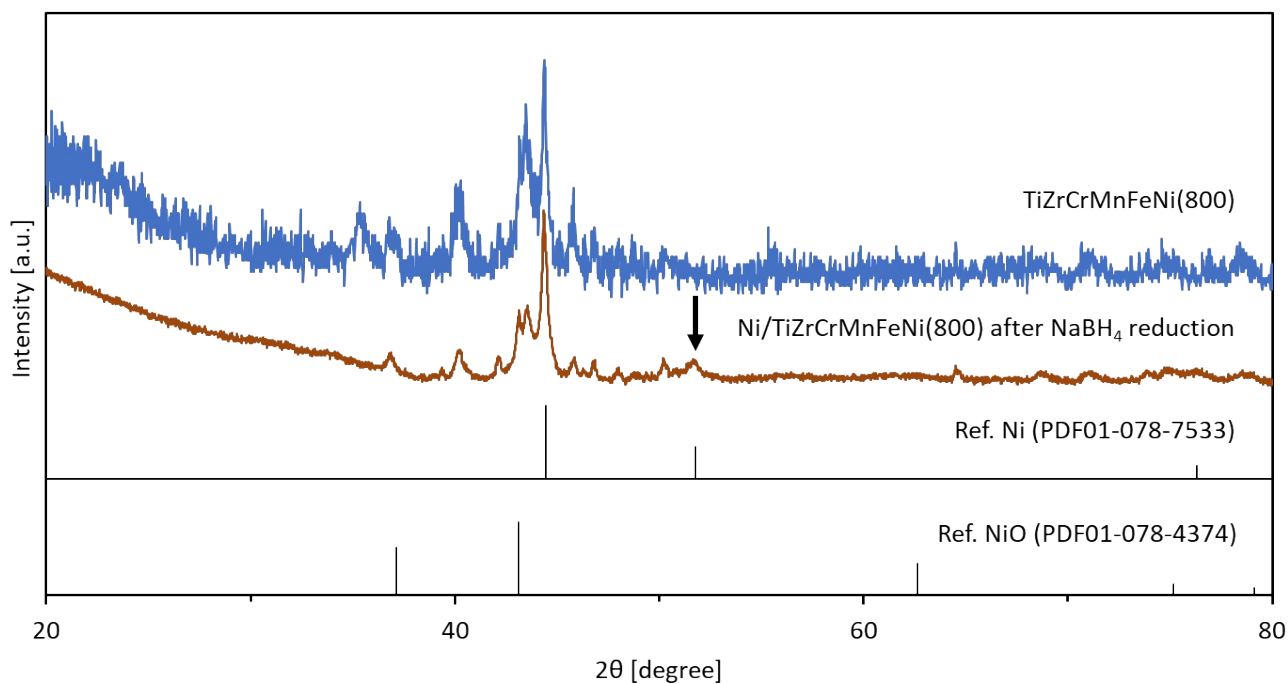


Fig. S5 XRD patterns for TiZrCrMnFeNi(800) and Ni/TiZrCrMnFeNi(800) after reduced by NaBH₄ at 25°C for 30 min with references of Ni and NiO. An arrow indicates a position of 51.8° corresponding to a signal for a (2 0 0) plane of metallic Ni.