

Nanostructured Ni-MoC_x: An efficient non-noble metal catalyst for the chemoselective hydrogenation of nitroaromatics

Yifei Zhang^{1,2,§}, Zhiwen Li^{2,6,§}, Jingjing Zhang², Liangliang Xu³, Zhong-Kang Han⁴ (✉), Alfons Baiker⁵ (✉), and Gao Li^{2,6} (✉)

¹ Institute of Catalysis for Energy and Environment, College of Chemistry and Chemical Engineering, Shenyang Normal University, Shenyang 110034, China

² State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

³ Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea

⁴ School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

⁵ Department of Chemistry and Applied Biosciences, Institute for Chemical and Bioengineering, ETH Zurich, Hönggerberg, HCI, Zurich CH-8093, Switzerland

⁶ University of Chinese Academy of Sciences, Beijing 100049, China

§ Yifei Zhang and Zhiwen Li contribute equally to this work.

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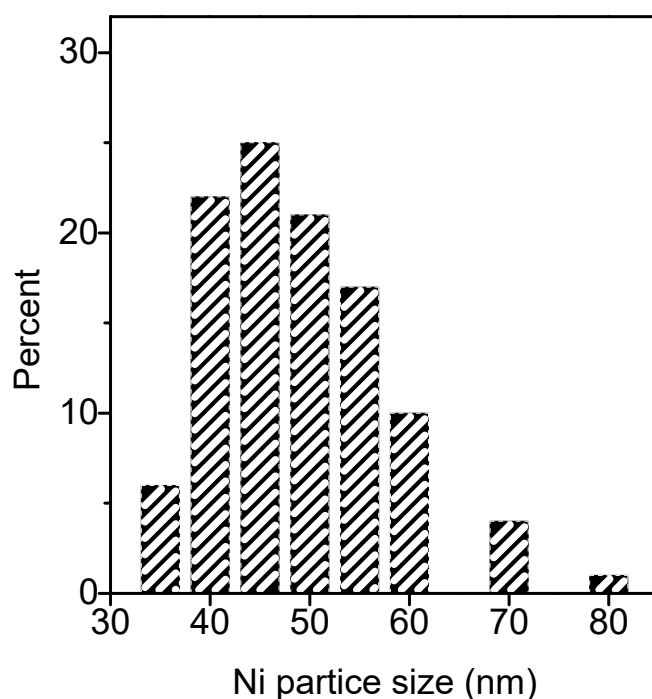


Figure S1 Size distribution of Ni particles in Ni-MoC_x nanocomposite. 97 Ni particles counted.

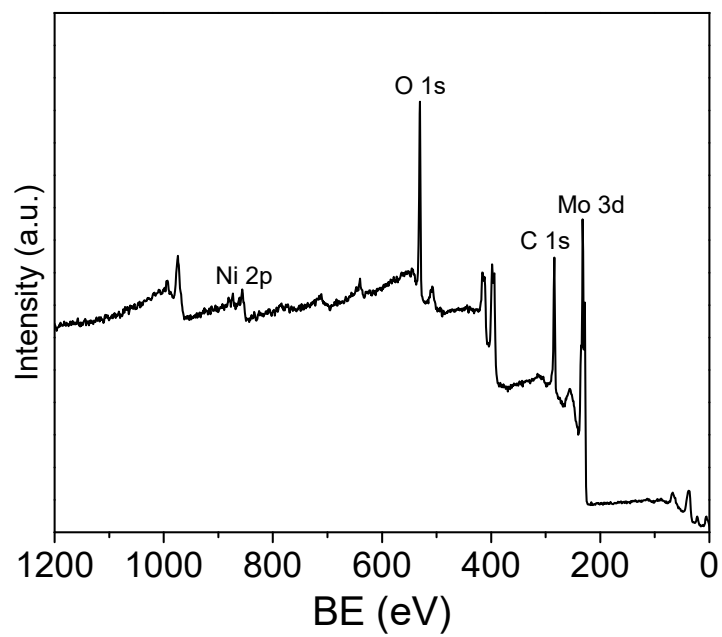


Figure S2 X-ray photoelectron survey spectrum of the Ni-MoC_x nanocomposite.

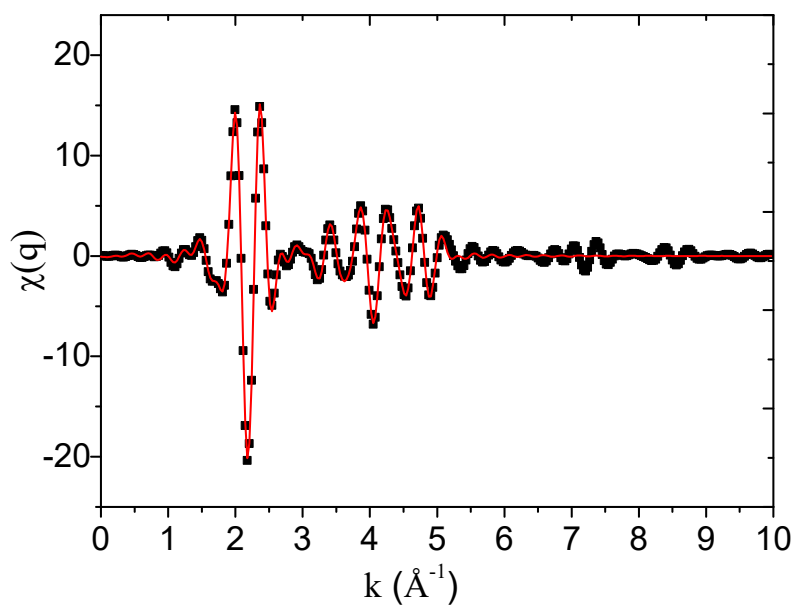


Figure S3 Ni K-edge EXAFS oscillation functions $k^3\chi(k)$ of Ni-MoC_x.

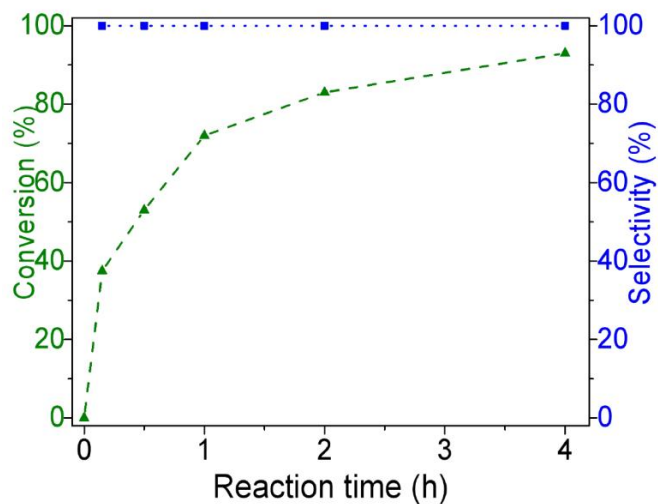


Figure S4 Conversion of nitrobenzene and selectivity to aminobenzene (aniline) as a function of reaction time over Ni-MoC_x catalyst. The reaction rate, expressed as TOF, of Ni-MoC_x nanocomposites reached 2390 mol_{PhNO₂} mol_{Ni}⁻¹ h⁻¹ at a reaction time of 9 min.

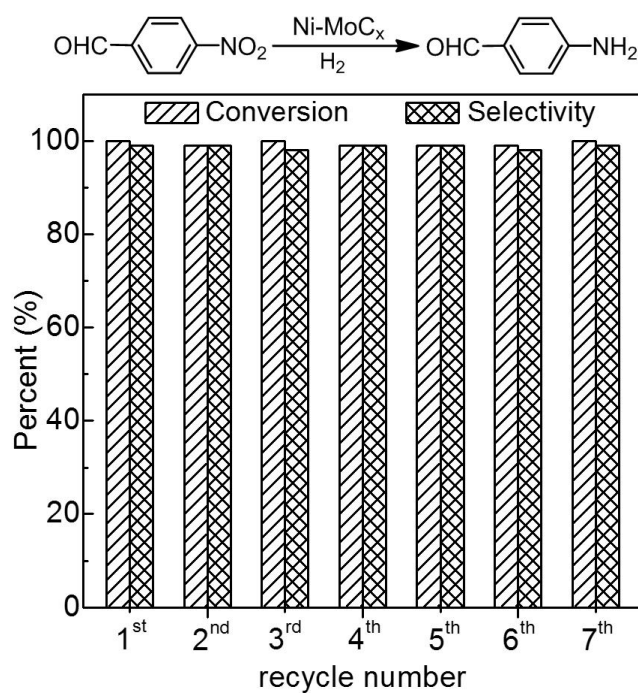


Figure S5 Recyclability of the Ni-MoC_x catalyst for the hydrogenation of 4-nitrobenzaldehyde. Reaction conditions: 5 mg catalysts, 50 mg 4-nitrobenzaldehyde, 2 mL H₂O, 2 MPa of H₂, at 140 °C for 10 h.

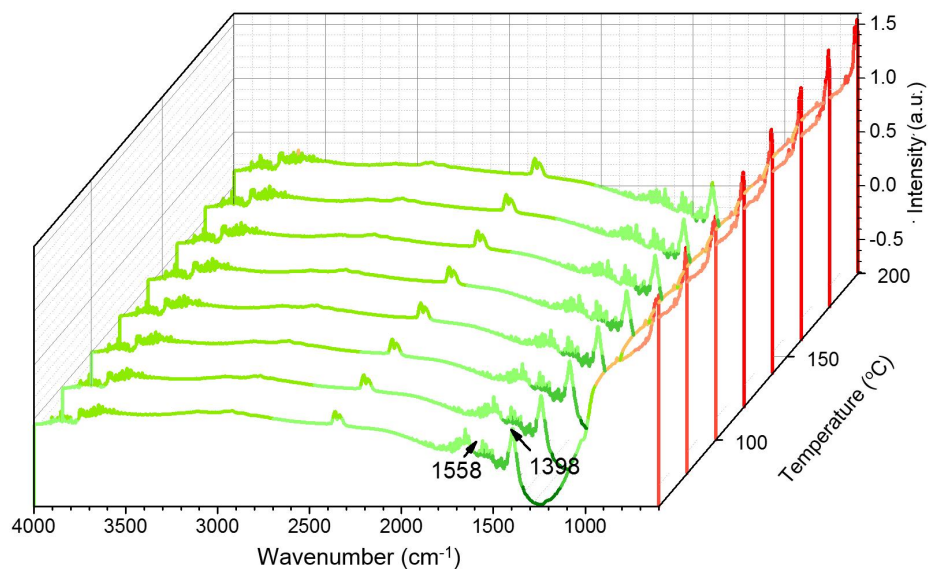


Figure S6 Temperature-dependent desorption of adsorbed nitrobenzene from Ni-MoC_x under He flow monitored by FT-IR. Conditions are given in Experimental section of the paper. The bands at ~ 1558 and 1398 cm^{-1} are assigned to the stretching vibration of the nitro group.

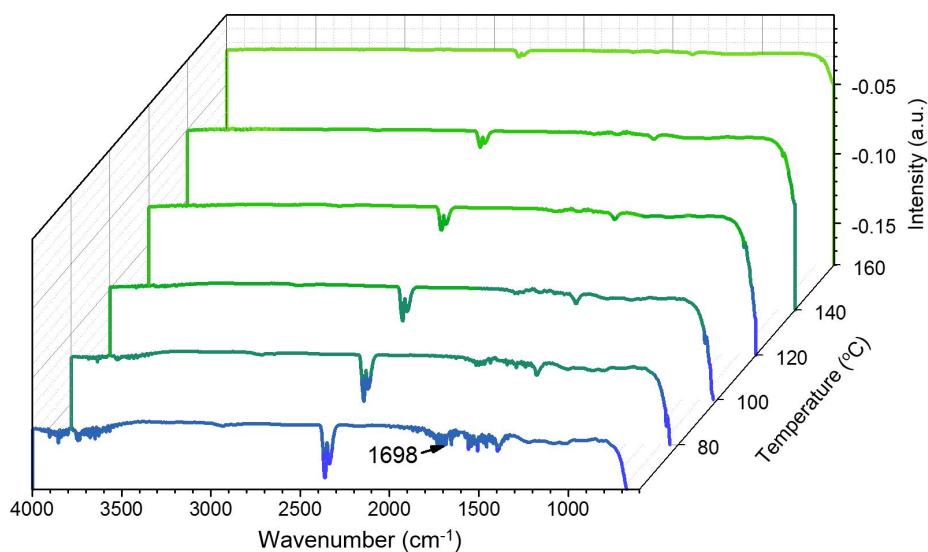


Figure S7 Temperature-dependent desorption of adsorbed benzaldehyde from Ni-MoC_x under He flow monitored by FT-IR. Conditions are given in Experimental section of the paper. The band at $\sim 1698\text{ cm}^{-1}$ is assigned to the stretching vibration of the carbonyl group.

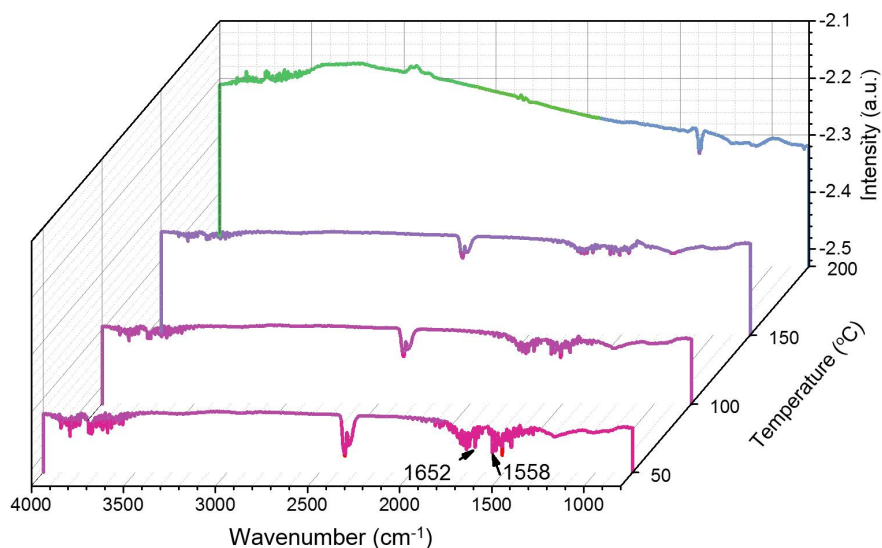


Figure S8 Temperature-dependent desorption of adsorbed 4-nitrobenzaldehyde from Ni-MoC_x under He flow monitored by FT-IR. Conditions are given in Experimental section of the paper. The bands at ~ 1558 and 1652 cm⁻¹ are assigned to the stretching vibration of the nitro and carbonyl groups, respectively.

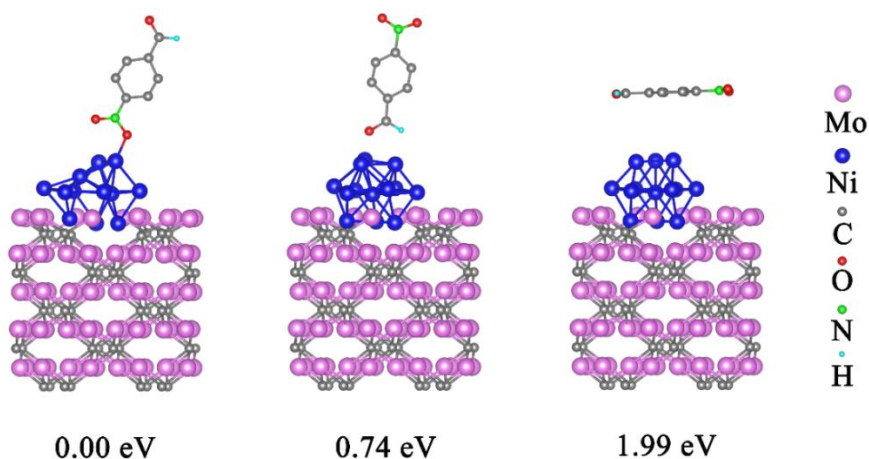


Figure S9 Configurations of the adsorbed 4-nitrobenzaldehyde onto Ni-Mo₂C composites. The energies are relative to the most stable configuration.

Table S1 Comparison of TOFs (h⁻¹) reported in the literature for various catalysts used for nitrobenzene hydrogenation^a

Catalysts		T (°C)	P _{H2} (MPa)	TOF (h ⁻¹)	Ref.
monometallic Noble metals	5%Pd/C	60	1.0	--	1
	Pd-B/SiO ₂	120	1.0	--	2
	Pd/LDH	50	1.0	70	3

	Pd/LDH-700	50	1.0	97	3
	Pd/C	50	1.0	109	3
	Pd/SiO ₂	50	1.0	115	3
	Pd/PEG	50	1.0	126	4
	Pd-PVA	50	2	250	5
	Pd/Ni foam	140	4.8	212	6
	Monolithic Ni@Pd	140	4.8	260	6
	Au/CeO ₂	100	1.0	--	7
	Au/TiO ₂	120	0.9	365	8
	Au/SiO ₂	120	0.9	20	8
	Ru@C ₆₀	50	3.0	56	9
Alloy	Au-Pd/Mo ₂ C	50	1.0	<90	10
Noble Metals ^b	cubic Pt ₃₄ Pd ₆₆	25	0.1	39168	11
	cubic Pt ₅₁ Pd ₄₉	25	0.1	60624	11
	cubic Pt ₆₇ Pd ₃₃	25	0.1	78132	11
Non-noble metals	LaCu _{0.67} Si _{1.33}	120	3	5084	12
	Co@CN	70	2	103	13
	Co@mesoNC	110	3	42	14
	FeSAs/Fe ₂ O ₃ ACs/NPC	30	N ₂ H ₄ ·H ₂ O ^c	1923	15
	γ-Fe ₂ O ₃ -UNSSs	80	N ₂ H ₄ ·H ₂ O ^c	32 mmol _{PhNO₂} h ⁻¹ g _{catal} ⁻¹	16
	Ni-phen@SiO ₂	60	1	77	17
	Ni-NiO/NGr@C	110	5	400	18
	Ni-SiCN	110	5	416	19
	Ni/SiO ₂	70	0.1	2.0	20
	Ni _{0.75} Fe _{0.25} /SiO ₂	70	0.1	11.4	20
	NiCu/C@SiO ₂	120	2	16740	21
	Ni-MoC _x	140	2	2390	This work

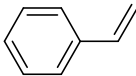
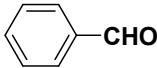
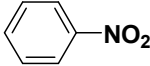
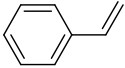
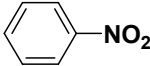
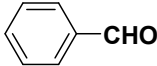
^a Note that the comparison of the TOFs achieved with the reported catalysts is impaired by the different conditions used (ethanol or water as solvent, temperature, and H₂ pressure). For detailed conditions and stability of the catalysts consult the cited references. ^b Single crystalline nanoparticles.

^c Reaction with N₂H₄ as reducing agent.

Table S2 Comparison of catalytic behavior of Ni-MoC_x and Ni@ZSM-5 reference catalyst in nitrobenzene and 4-nitrobenzaldehyde hydrogenation reactions. Reaction conditions: 5 mg catalysts, 50 mg substrates, 2 mL H₂O, 2 MPa H₂, at 140 °C for 4 h

Catalyst	Substrate	Conversion	Selectivity
Ni@ZSM-5	nitrobenzene	56%	>99%
Ni-MoC _x		93%	>99%
Ni@ZSM-5	4-nitrobenzaldehyde	27%	56%
Ni-MoC _x		56%	>99%

Table S3 Control experiments with styrene, benzaldehyde, and nitrobenzene substrates over Ni-MoC_x catalyst

Entry	Conversion (%)					
	styrene	benzaldehyde	nitrobenzene			
1 ^a	-		-	85	-	-
2 ^a	-	-		-	100	-
3 ^b			-	0.8	-	80
4 ^b		-		-	5	77

Reaction conditions: 5 mg Ni-MoC_x catalysts, 2 mL H₂O, 2 MPa of H₂, 140 °C, 10 h. ^a0.4 mmol of styrene or benzaldehyde. ^b0.4 mmol of styrene or benzaldehyde and 0.4 mmol of nitrobenzene.

Table S4 Bader charge (e) of Ni-Mo₂C

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Bader charge	Atom	<i>x</i>	<i>y</i>	<i>z</i>	Bader charge
Mo	3.796	4.903	4.567	-0.780	C	3.799	1.388	1.018	0.944
Mo	3.749	4.884	9.260	-0.775	C	3.801	1.389	5.741	1.537
Mo	5.345	2.282	4.600	-0.797	C	3.795	1.370	10.540	1.487
Mo	5.287	2.247	9.258	-0.818	C	5.343	4.009	3.395	1.534
Mo	3.796	3.115	2.223	-0.834	C	5.313	4.016	8.099	1.510
Mo	3.777	3.120	6.962	-0.740	C	2.304	4.009	1.018	0.947
Mo	3.966	3.191	11.551	-0.746	C	2.292	4.014	5.746	1.532
Mo	5.345	0.494	2.190	-0.830	C	2.267	4.006	10.561	1.480
Mo	5.310	0.517	6.936	-0.753	C	0.761	1.388	3.395	1.534
Mo	5.405	0.494	11.567	-0.339	C	0.766	1.387	8.106	1.518
Mo	2.307	0.494	2.223	-0.846	C	9.875	1.388	1.018	0.945
Mo	2.310	0.502	6.956	-0.753	C	9.890	1.394	5.756	1.524
Mo	2.183	0.528	11.570	-0.503	C	9.902	1.420	10.529	1.473
Mo	0.758	3.115	2.190	-0.824	C	11.419	4.009	3.395	1.535
Mo	0.758	3.132	6.924	-0.755	C	11.422	4.021	8.109	1.520
Mo	0.684	3.025	11.510	-0.233	C	8.381	4.009	1.018	0.945
Mo	2.307	2.282	4.567	-0.804	C	8.375	4.013	5.749	1.528
Mo	2.281	2.260	9.322	-0.782	C	8.361	3.986	10.428	1.321
Mo	0.758	4.903	4.600	-0.799	C	6.837	1.388	3.395	1.538
Mo	0.742	4.911	9.360	-0.756	C	6.841	1.405	8.095	1.491
Mo	9.873	4.903	4.567	-0.781	C	3.799	6.630	1.018	0.942
Mo	9.903	4.962	9.279	-0.769	C	3.816	6.638	5.750	1.525
Mo	11.422	2.282	4.600	-0.804	C	3.820	6.618	10.496	1.390
Mo	11.457	2.306	9.362	-0.794	C	5.343	9.251	3.395	1.533
Mo	9.873	3.115	2.223	-0.833	C	5.339	9.264	8.115	1.513
Mo	9.883	3.143	6.953	-0.761	C	2.304	9.251	1.018	0.950
Mo	9.977	3.277	11.588	-0.614	C	2.291	9.250	5.751	1.535
Mo	11.422	0.494	2.190	-0.826	C	2.281	9.223	10.588	1.492
Mo	11.432	0.511	6.917	-0.758	C	0.761	6.630	3.395	1.537
Mo	11.433	0.444	11.516	-0.264	C	0.778	6.629	8.108	1.512
Mo	8.383	0.494	2.223	-0.845	C	9.875	6.630	1.018	0.940
Mo	8.384	0.524	6.951	-0.765	C	9.892	6.645	5.754	1.526
Mo	8.233	0.672	11.580	-0.672	C	9.882	6.678	10.559	1.395
Mo	6.835	3.115	2.190	-0.830	C	11.419	9.251	3.395	1.537

Mo	6.833	3.132	6.910	-0.749	C	11.395	9.258	8.101	1.522
Mo	8.383	2.282	4.567	-0.787	C	8.381	9.251	1.018	0.945
Mo	8.416	2.261	9.257	-0.795	C	8.358	9.256	5.753	1.529
Mo	6.835	4.903	4.600	-0.800	C	8.385	9.301	10.567	1.460
Mo	6.862	4.847	9.241	-0.925	C	6.837	6.630	3.395	1.531
Mo	3.796	10.144	4.567	-0.785	C	6.852	6.642	8.138	1.527
Mo	3.806	10.114	9.337	-0.759	Ni	6.842	3.068	11.255	0.015
Mo	5.345	7.524	4.600	-0.799	Ni	5.393	5.653	11.220	-0.004
Mo	5.370	7.564	9.357	-0.810	Ni	8.304	5.721	11.272	-0.286
Mo	3.796	8.357	2.223	-0.837	Ni	6.811	4.833	13.034	-0.057
Mo	3.781	8.367	6.963	-0.757	Ni	5.696	2.501	13.232	0.223
Mo	3.934	8.336	11.640	-0.607	Ni	8.209	2.702	13.261	0.213
Mo	5.345	5.736	2.190	-0.831	Ni	9.520	4.962	13.296	0.195
Mo	5.358	5.757	6.928	-0.760	Ni	8.154	7.133	13.124	0.226
Mo	2.307	5.736	2.223	-0.842	Ni	5.616	7.055	13.218	0.223
Mo	2.324	5.746	6.968	-0.757	Ni	4.256	4.916	13.272	0.227
Mo	2.349	5.761	11.649	-0.616	Ni	5.654	5.540	15.041	0.064
Mo	0.758	8.357	2.190	-0.830	Ni	7.968	5.669	14.941	0.029
Mo	0.732	8.372	6.918	-0.766	Ni	6.879	3.544	15.013	0.049
Mo	0.643	8.216	11.489	-0.149	Mo	8.378	5.754	6.957	-0.739
Mo	2.307	7.524	4.567	-0.793	Mo	6.835	8.357	2.190	-0.830
Mo	2.290	7.542	9.282	-0.766	Mo	6.839	8.366	6.932	-0.758
Mo	0.758	10.144	4.600	-0.805	Mo	6.713	8.497	11.541	-0.390
Mo	0.741	10.155	9.370	-0.782	Mo	8.383	7.524	4.567	-0.790
Mo	9.873	10.144	4.567	-0.784	Mo	8.405	7.573	9.294	-0.772
Mo	9.870	10.146	9.308	-0.762	Mo	6.835	10.144	4.600	-0.795
Mo	11.422	7.524	4.600	-0.797	Mo	6.834	10.179	9.318	-0.758
Mo	11.476	7.557	9.340	-0.802	Mo	11.422	5.736	2.190	-0.827
Mo	9.873	8.357	2.223	-0.833	Mo	11.442	5.750	6.916	-0.760
Mo	9.836	8.376	6.969	-0.765	Mo	11.398	5.701	11.590	-0.310
Mo	9.981	8.419	11.634	-0.596	Mo	8.383	5.736	2.223	-0.842

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