Electronic Supplementary Information

Reverse Hydrogen Spillover in Supported Subnanosize Clusters of the Metals of Groups 8 to 11. A Computational Model Study

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Table S4. Number of unpaired electrons Ns and interatomic distances (in pm) in the optimized structures of the gas phase metal clusters in C_3 symmetry.

	Ns[c]	$R(M_a\text{-}M_a)$[a]		$R(M_a\text{-}M_b)$[b]	
Fe	20	230	230	251	251
Co	14	230	230	239	239
Ni	8	234	238	234	235
Cu	2	245	245	240	241
Ru	4	252	252	245	245
Rh	0	249	249	248	248
Pd	2	267	267	266	266
Ag	2	273	273	291	292
Os	8	243	243	249	249
Ir	0	251	251	252	252
Pt	0	259	259	263	263
Au	0	279		263	263

[a] Distance between metal atoms in one of the basic triangles.

[b] Distance between metal atoms belonging to different basic triangles.

Table S5. Mulliken charges (in e) of the O centers[a] of the six-ring in models[b] of zeolite-supported bare metal clusters (M_6) and clusters with hydrogen impurities (M_6H_3)

	M_6/Zeo(3H)		M_6(3H)/Zeo	
	O_M	O_H	O_M	O_H
Fe	-0.72	-0.63	-0.72	-0.72
Co	-0.72	-0.63	-0.71	-0.71
Ni	-0.70	-0.63	-0.71	-0.70
Cu	-0.72	-0.63	-0.71	-0.72
Ru	-0.59	-0.63	-0.66	-0.67
Rh	-0.64	-0.54	-0.71	-0.71
Pd	-0.60	-0.60	-0.65	-0.65
Ag	-0.57[c]	-0.60	-0.68	-0.67
Os	-0.59[c]	-0.62	-0.67	-0.67
Ir	-0.51	-0.62	-0.63	-0.63
Pt	-0.58	-0.62	-0.62	-0.63
Au	-0.57[c]	-0.60	-0.62	-0.68[c]

[a] O_M – oxygen centers of the zeolite fragment not participating in OH bonds, i.e. all centers of the models M_6(3H)/Zeo, O_M – oxygen centers of the zeolite fragment participating in OH bonds, in the models M_6/Zeo(3H)

[b] See text and Fig. 1.

[c] Oxygen centers of the zeolite fragment which do neither participate in the bridging OH groups nor are bound to the metal cluster.

Table S6. Estimated binding energy shifts[a] of the 1s level of the oxygen centers[b] of the zeolite fragment and their variations[c] for zeolite-supported bare metal clusters (M_6) and clusters with hydrogen impurities (M_6H_3).

	M_6/Zeo(3H)				M_6(3H)/Zeo				Comparison
	O_M	O_H	$\langle\Delta E_O\rangle$	Δ^2E_O	O_M	O_H	$\langle\Delta E_O\rangle$	Δ^2E_O	$\Delta\langle\Delta E_O\rangle$
Fe	-0.08	-0.23	-0.16	1.63	-0.26	-2.10	-1.18	0.06	-1.02
Co	-0.07	-0.19	-0.13	1.66	-0.23	-2.08	-1.16	0.07	-1.03
Ni	-0.10	-0.18	-0.14	1.70	-0.18	-2.02	-1.10	0.06	-0.96
Cu	-0.23	0.00	-0.12	2.01	-0.61	-2.37	-1.49	0.02	-1.38
Ru	-0.31	-0.68	-0.50	1.41	0.02	-1.56	-0.77	0.20	-0.27
Rh	-0.72	-0.49	-0.61	2.01	-0.19	-2.00	-1.10	0.03	-0.49
Pd	-0.21	0.03	-0.09	2.02	-0.01	-1.77	-0.89	0.02	-0.80
Ag	-0.66[d]	0.19	-0.24	2.63	-0.72	-2.51	-1.62	0.01	-1.38
Os	-0.38[d]	-0.60	-0.49	1.56	0.77	-0.96	-0.10	0.05	0.39
Ir	0.39	0.24	-0.31	1.63	0.70	-1.05	-0.18	0.03	-0.49
Pt	0.47	0.36	-0.41	1.67	0.61	-1.18	-0.29	0.01	-0.70
Au	0.44[d]	0.34	-0.05	2.56	-1.26	-1.96[d]	-1.61	1.08	-1.56

[a] See text for the reference values used to estimate the core level shifts.

[b] O_M – oxygen centers of the zeolite fragment not participating in OH bonds, i.e. all centers of the models M_6(3H)/Zeo, O_M – oxygen centers of the zeolite fragment participating in OH bonds, in the models M_6(3H)/Zeo

[c] $\langle\Delta E_O\rangle$ – average of core level shifts over O_M and O_H atoms, Δ^2E_O – difference between ΔE_O values of both oxygen centers (Δ^2E_O = 1.78 eV for the isolated zeolite fragment), $\Delta\langle\Delta E_O\rangle$ – difference between the $\langle\Delta E_O\rangle$ values of bare adsorbed metal clusters and adsorbed clusters with hydrogen impurities (a negative value implies destabilization of the core levels due to the reaction).

[d] Levels corresponding to the oxygen centers of the zeolite fragment which do neither participate in the bridging OH groups nor are bound to the metal cluster.