The Electronic Supplementary Information

Size and structure effects on platinum nanocatalysts: Theoretical insights from methanol dehydrogenation

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CONTENT

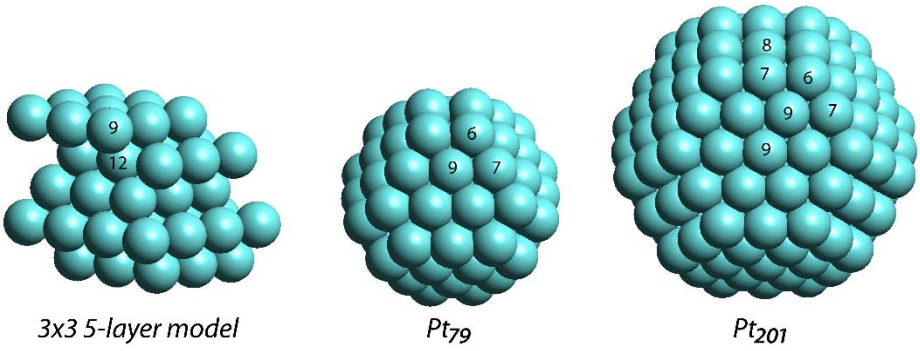

Figure S1. Regular coordination numbers of surface atoms on ideal Pt(111) and model NPs: 12 at bulk, 9 at a surface and (111) nanofacet, 8 at (100) nanofacet, 7 at edges, 6 at corners.

Table S1. Adsorption energies, E_{ads} (in kJ mol^{-1}), of methanol, formyl and carbon monoxide on 5-layer Pt(111) slab calculated with different k-point meshes. On-top binding to the surface Pt atom by the carbon center of the adsorbed species in all cases.

k-point mesh	$E_{ads}(CH_3OH)$	$E_{ads}(CHO)$	$E_{ads}(CO)$
4×4×1	-34.12	-243.16	-164.61
5×5×1	-33.89	-242.36	-164.90
7×7×1	-33.42	-242.44	-164.64

Table S2. CO bond lengths (in Å) in different adsorption complexes at Pt(111), Pt_{79} and Pt_{201} NPs, corrections Δ for the CO adsorption energy estimated by formula $\Delta=460d_{CO}-518$ (in kJ mol^{-1}) [V. Sumaria, L. Nguyen, F.F. Tao, P. Sautet, *ACS Catal*., 2020, **10**, 9533-9544], CO adsorption energies without and with correction Δ (in kJ mol^{-1}).

Site	d_{CO}	**Δ**	E_{ads}	E_{ads}+**Δ**
free CO	1.1416			
Pt_{79}-*t*	1.1577	14.69	–180	–166
Pt_{79}-t_e	1.1600	15.735	–200	–184
Pt_{79}-t_v	1.1604	15.942	–211	–195
Pt_{79}-*br* (*t*-*t*)	1.1827	26.192	–209	–182
Pt_{79}-br_e (*t*-t_e)	1.1840	26.795	–188	–161
Pt_{79}-$br_e^{111/111}$ (t_v-t_e)	1.1836	26.625	–219	–193
Pt_{79}-$br_e^{111/100}$ (t_v-t_e)	1.1790	24.508	–186	–161
Pt_{79}-*fcc* (three-fold hollow)	1.1945	31.629	–209	–177
Pt_{79}-*4-hold*	1.1966	32.591	–211	–178
Pt_{201}-t_1	1.1563	14.022	–148	–134
Pt_{201}-t_2	1.1572	14.46	–164	–150
Pt_{201}-t_v	1.1603	15.873	–199	–183
Pt_{201}-br_e (t_v-t_e)	1.1828	26.252	–188	–162
Pt(111)-*t*	1.1557	13.765	–165	–151
Pt(111)-*br*	1.1812	25.493	–173	–148
Pt(111)-*fcc*	1.1936	31.228	–176	–145
Pt(111)-*hcp*	1.1930	31.118	–174	–143

Table S3. Energies (kJ mol^{-1}) of CH_3OH adsorption at different sites of Pt(111), Pt_{79} and Pt_{201} NPs.

Site	$E_{ads}(CH_3OH)$
Pt_{79}-*t*	–45
Pt_{79}-t_e	–48
Pt_{79}-t_v	–56
Pt_{201}-t_1	–19
Pt_{201}-t_v	–57
Pt(111)-*t*	–34

Table S4. Energies (kJ mol^{-1}) of CH_3O adsorption at different sites of Pt(111), Pt_{79} and Pt_{201} NPs.

Site	$E_{ads}(CH_3O)$
Pt_{79}-*t*	–193
Pt_{79}-t_e	–204
Pt_{79}-t_v	–225
Pt_{79}-$br_e^{111/111}$	–221
Pt_{79}-$br_e^{111/100}$	–228
Pt_{79}-*br*	–174
Pt_{201}-t_1	–162
Pt_{201}-t_v	–217
Pt(111)-*t*	–173
Pt(111)-*br*	–169
Pt(111)-*fcc*	–165

Table S5. Energies (kJ mol^{-1}) of CH_2O adsorption at different sites of Pt(111), Pt_{79} and Pt_{201} NPs.

Site	$E_{ads}(CH_2O)$
Pt_{79}-t_v(O)–t_e(C)	–123
Pt_{79}-t_v(C)–t_e(O)	–115
Pt_{79}-t_v(C)–t_v(O)	–105
Pt_{79}-t(C)–t_e(O)	–86
Pt_{79}-$br_v(t_vt)$(O)–t_e(C)	–103
Pt_{79}-t(O)–t(C)	–76
Pt_{79}-t_v(O)–t(C)	–107
Pt_{79}-t_v(C)–t(O)	–81
Pt_{201}-t_1(O)–t_2(C)	–48
Pt_{201}-t_v(O)–t_e(C)	–108
Pt(111)-t(O)–t(C)	–56
Pt(111)-t(O)	–26

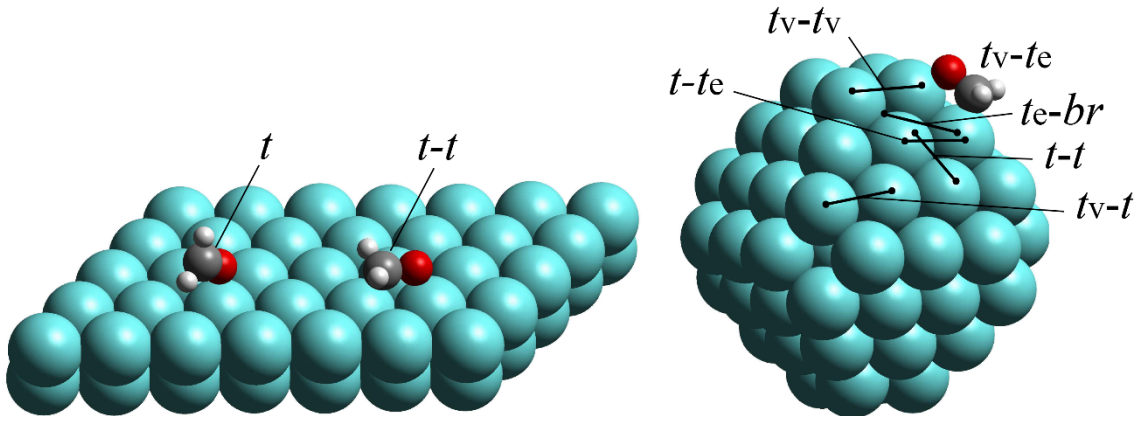

Figure S2. The formaldehyde structures on Pt(111) and Pt_{79}.

Table S6. Energies (kJ mol^{-1}) of CHO adsorption at different sites of Pt(111), Pt_{79} and Pt_{201} NPs.

Site	$E_{ads}(CHO)$
Pt_{79}-t_v(O)–t_e(C)	–285
Pt_{79}-t_v(C)–t_e(O)	–289
Pt_{79}-t_v(C)	–265
Pt_{79}-t(C)	–271
Pt_{79}- t(O)–br(C)	–261
Pt_{79}-t(O)–$br_e^{111/100}$(t_v-t_v)(C)	–228
Pt_{79}-t(O)–$br_e^{111/111}$(t_v–t_e)(C)	–262
Pt_{79}-t(O)–br_e(t_e-t)(C)	–235
Pt_{79}-t_e(O)–t(C)	–261
Pt_{201}-t_1(C)	–251
Pt_{201}-t_2(C)	–252
Pt_{201}-t_v(O)–t_e(C)	–275
Pt(111)-br(C)–t(O)*	–237
Pt(111)-t(C)	–243

*above fcc-site

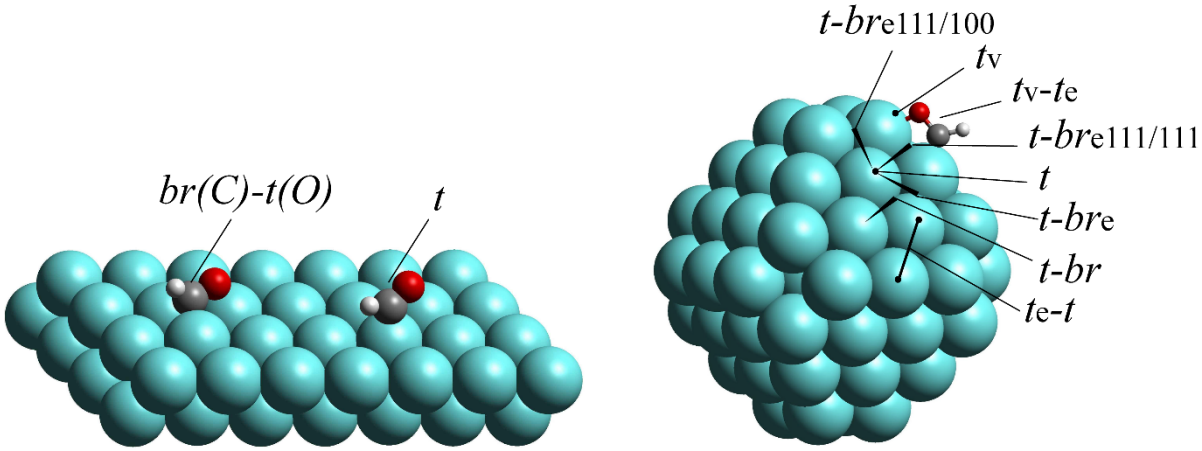

Figure S3. The formyl structures on Pt(111) and Pt_{79}.

Table S7. Energy (kJ mol^{-1}) of adsorption of H atom at different sites of Pt(111), Pt_{79} and Pt_{201} NPs.

Site	$E_{ads}(H)$
Pt_{79}-*t*	–285
Pt_{79}-t_e	–266
Pt_{79}-t_v	–271
Pt_{79}-br_e (t_{br}-*t*)	–267
Pt_{79}-$br_e^{111/100}$ (t_v-t_v)	–275
Pt_{79}-$br_e^{111/111}$ (t_v-t_e)	–285
Pt_{79}-fcc_1 (three-fold hollow)	–267
Pt_{79}-fcc_2	–267
Pt_{201}-t_1	–270
Pt_{201}-t_v	–260
Pt(111)-*t*	–267
Pt(111)-*br*	–263
Pt(111)-*fcc*	–267
Pt(111)-*hcp*	–263

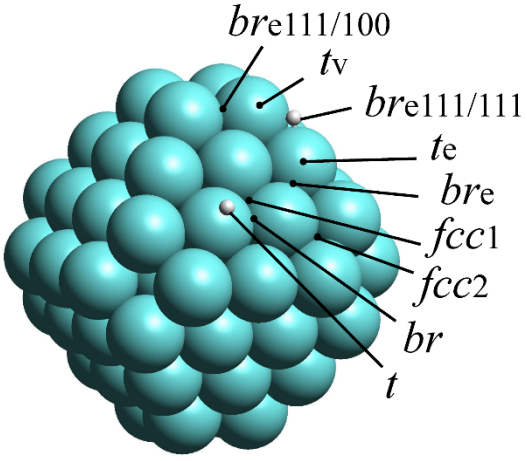

Figure S4. The H adsorption sites on Pt_{79}.

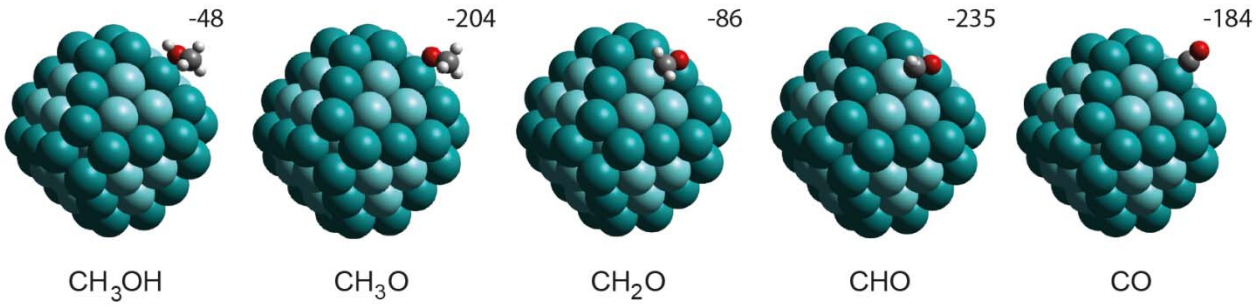

Figure S5. Intermediates of methanol dehydrogenation calculated at the edge of Pt_{79} NP. Adsorption energies (in kJ mol^{-1}) are given nearby the corresponding structures. H atoms are colored white, C atoms – gray, O atoms – red, Pt atoms – cyan.

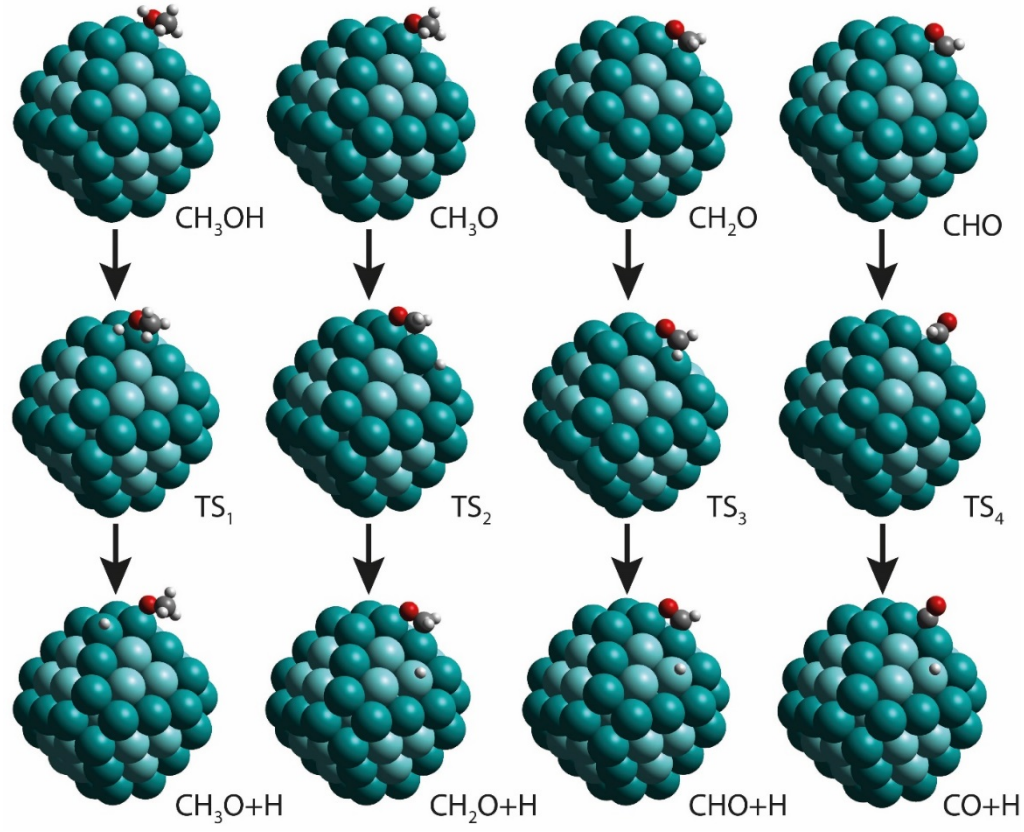

Figure S6. Elementary steps of methanol dehydrogenation at corner site of Pt_{79} NP. H atoms are colored white, C atoms – gray, (edge) O atoms – red, Pt atoms – cyan.