Title: “Hydrogenolysis of aniline on transition metal surfaces: effects of temperature and electronic structure”

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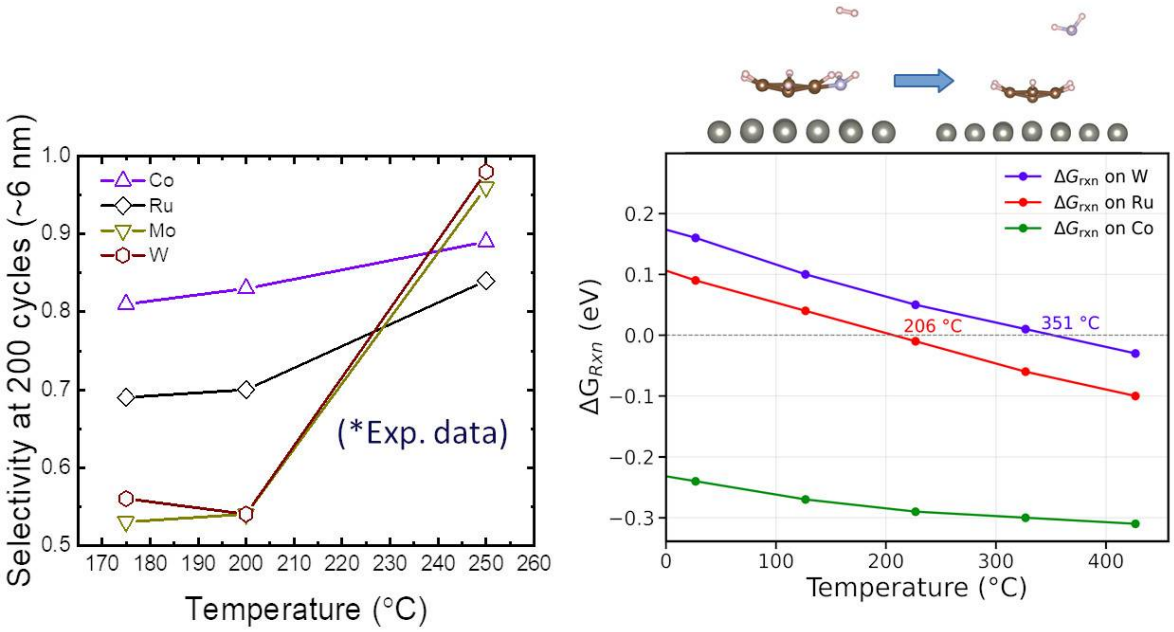

Figure S1. Experimental selectivity as a function of temperature (left) measured after 200 ABC cycles (corresponding to a nominal thickness of 6 nm) on substrates of Co, Ru, Mo, and W. At ~175 °C, Co (S ≈ 0.80) and Ru (S ≈ 0.70) exhibit higher selectivity than W and Mo (S ≈ 0.55). As the temperature increases to ~250 °C, the selectivity for W and Mo increases sharply to S > 0.95, while Co and Ru show only moderate changes. The right panel shows the Gibbs free energy of the overall aniline hydrogenolysis reaction (ΔG_{Rxn}), producing benzene and NH_3, on Co, Ru, and W as a function of temperature, obtained from DFT. ΔG_{Rxn} is negative for Co across the entire temperature range, goes to negative for Ru around ~250 °C and remains positive for W up to ~350 °C.

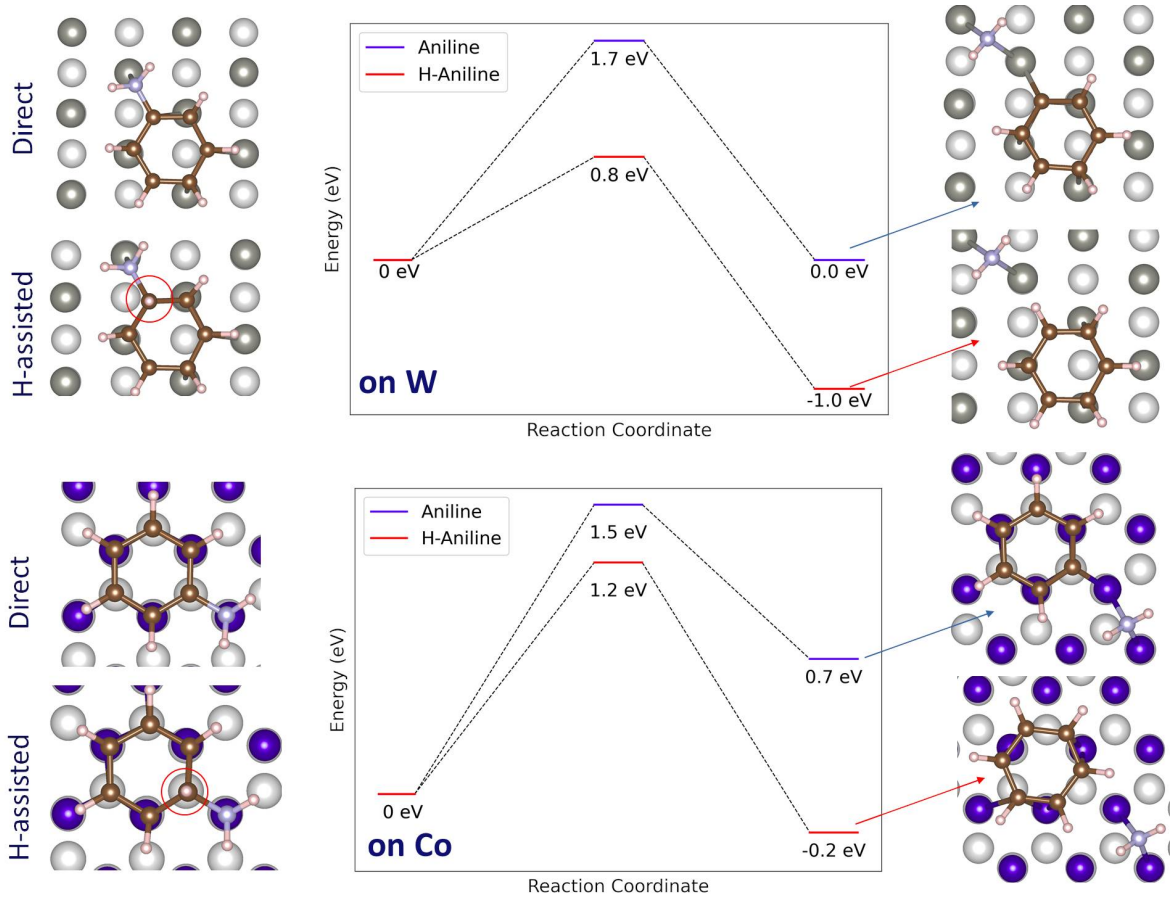

Figure S2. Reaction coordinate of the comparison of direct (blue lines) and hydrogen-assisted (red line) C–N cleavage on W (top) and Co (bottom), calculated with DFT. Energies are referenced to adsorbed intact aniline. For W, the direct pathway exhibits an activation barrier of ~1.7 eV, which is reduced to ~0.8 eV after hydrogenation, and the reaction becomes exothermic. For Co, the direct pathway barrier is ~1.5 eV and is reduced to ~1.2 eV in the hydrogen-assisted pathway, which also renders the reaction exothermic. These data demonstrate that hydrogenation reduces the C-N cleavage barrier in both metals, with a substantially greater effect on W.