Supplementary Material for PCCP

Cobalt in $NaBH_4$ hydrolysis

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Experimental

Materials. Cobalt chloride ($CoCl_2$, Acros Organics), cobalt nitrate ($Co(NO_3)_2$, Acros Organics), cobalt oxide (Co_3O_4, Sigma-Aldrich) and cobalt hydroxide ($Co(OH)_2$, Sigma-Aldrich) were used as Co catalyst precursors. Sodium borohydride ($NaBH_4$, Sigma-Aldrich) and the Co precursors were used as received, stored and handled in an Ar-filled glove box.

Synthesis of the black solid showed in Figure 2. Solid $NaBH_4$ and solid $CoCl_2$ (equiv. of 200 mg of Co) were mixed together in a mortar. The weight ratio $NaBH_4$/Co was 9. The homogeneous mixture (the homogeneousness being characterized by a uniform sky blue color) was then transferred in an Ar-filled Schlenk glassware and closed by a silicon stopper. The Schlenk glassware was immersed in an ice bath to avoid vigorous H_2 evolution. An excess of water (mol ratio $H_2O/NaBH_4$ of 100) was then injected. No NaOH was used. Upon the hydrolysis completion, the dark grey solid consisting of the black solid and borates was washed thoroughly 5 times with water under Ar (till the washing water reached neutral pH) to remove the borates and chlorides. Then, it was dried under vacuum overnight. The black solid was stored in the glove box.

Synthesis of the used catalysts showed in Figure 4. In the Ar-filled glove box, $CoCl_2$, $Co(NO_3)_2$, Co_3O_4 and $Co(OH)_2$ were weighted and each was transferred into a Schlenk glassware which was closed by a silicon stopper. A stabilized solution of $NaBH_4$ was prepared: [NaOH] = 0.1 M, [$NaBH_4$] = 3 M. Distilled water was purged with Ar to remove O_2. The mol ratios were as follows: $BH_4^-/Co = 14$, $BH_4^-/OH^- = 30$, $BH_4^-/H_2O = 18$. To start H_2 generation, the BH_4^- solution was injected onto the catalyst. The experiment was carried on at 20 °C. The used Co catalysts were recovered by thorough washing (till the washing water reached neutral pH) and drying under vacuum. The as-obtained used catalysts were stored in the glove box and then characterized by XRD. Afterwards, the solids were annealed at 500 °C under Ar for 2 h, the heating rate being set at 5 °C min^{-1}, to be once more analyzed by XRD.

Experimental conditions in which the black/blue/brown solid forms. This study had as objective to define the concentrations (or mol ratios BH_4^-/OH^-) in which the black solid forms from either $CoCl_2$ or $Co(NO_3)_2$. The tests were performed at near 0 °C (tubes immersed in ice bath) to make the Co precursors reduction slower. To set the experimental conditions in which the study will have been done an optimization pre-study was performed. The concentration of the Co salt was set at 0.02 M. The concentration of NaOH was set at 0.1 M. The $NaBH_4$ concentration was varied from 2.10^{-8} to 2 M (i.e. mol ratios BH_4^-/Co^{2+} from 10^{-6} to 10^2). The evolutions in the solutions were tracked visually as well as by UV. In each case, the solution evolved as follows. After injection of the $NaBH_4$ solution in the pink Co^{2+} solution, the solution turned to blue with formation of very small blue albumin-like aggregates within the 1st min. The color progressively changed, turning to light green at around 1 min, yellow at around 2 min and beige at 3 min. Finally, a brown albumin-like precipitate formed. Afterwards, the NaOH concentration was varied from 0 to 1 M, the concentrations of Co^{2+} and BH_4^- being kept at 0.02 M. It was observed that within this NaOH concentration range, a black solid, a stable blue solution or a brown albumin-like precipitate could form. Hence, the study focused on the following experimental conditions: mol ratios Co^{2+}/BH_4^- of 1 and BH_4^-/OH^- from 0.2 to $+\infty$.

Synthesis of the brown precipitates showed in Figures 6 and 7. The brown albumin-like precipitates were synthesized in much larger scale to be isolated and characterized by XRD and IR. An equivalent of 200 mg of Co was weighted from $CoCl_2$ and $Co(NO_3)_2$ under Ar to have a solution such as $[Co^{2+}]$ = 0.02 M. A stabilized solution ([NaOH] = 0.1 M) of $NaBH_4$ such as mol ratio Co^{2+}/BH_4^- = 1 was injected in the Co^{2+} solution. The mixing was directly done in several tubes (of 50 mL) dedicated to centrifugation. After few min, i.e. once the brown albumin-like precipitates started to form, the solutions were centrifugated at 10000 rpm for 10 min. The excess of water was removed with a syringe while keeping the solid under a 3-5 mm H_2O film. The tubes were transferred in a 500 mL flask to be dried under vacuum overnight. The solids were then recovered in the Ar-filled filled glove box.

X-Ray Diffraction. Whatever the solid to be characterized by XRD (Bruker D5005 powder diffractometer, CuKα radiation λ = 1.5406 Å), it was always prepared as follows. The solids obtained above were stored in the Ar-filled glove box. The XRD support was adapted to protect the sample using a kapton film (and a rubber seal), which efficiently avoided the sample to have any contact with air and moisture during the XRD. The XRD was carried on from 10 to 90 °.

IR spectroscopy. Samples were analyzed by diffuse reflectance Fourier transform infrared spectroscopy (IR, FTIR Nicolet 380).

UV spectroscopy. For one solution, 5 UV spectra (UV mc^2 safas monaco) were collected for 5 min, i.e. 1 spectrum per min. The Co^{2+} solution at near 0 °C was injected into a quartz cell under stirring. Then, the stabilized $NaBH_4$ solution at near 0 °C was injected while the UV absorption data collecting was started. The solution was kept under stirring during the whole UV experiment.

Figure S1.

Reduction of Co^{2+} from $CoCl_2$ (top scheme) or $Co(NO_3)_2$ (bottom scheme) (mol ratio Co^{2+}/BH_4^- of 1) as a function of the mol ratio BH_4^-/OH^-.

Figure S2.

UV spectra recorded during the 1st 5 min of the reduction of Co^{2+} (from $CoCl_2$) by BH_4^- to have one spectrum per min: 1st min (diamond), 2nd min (square), 3rd min (triangle), 4th min (circle), 5th min (dash).

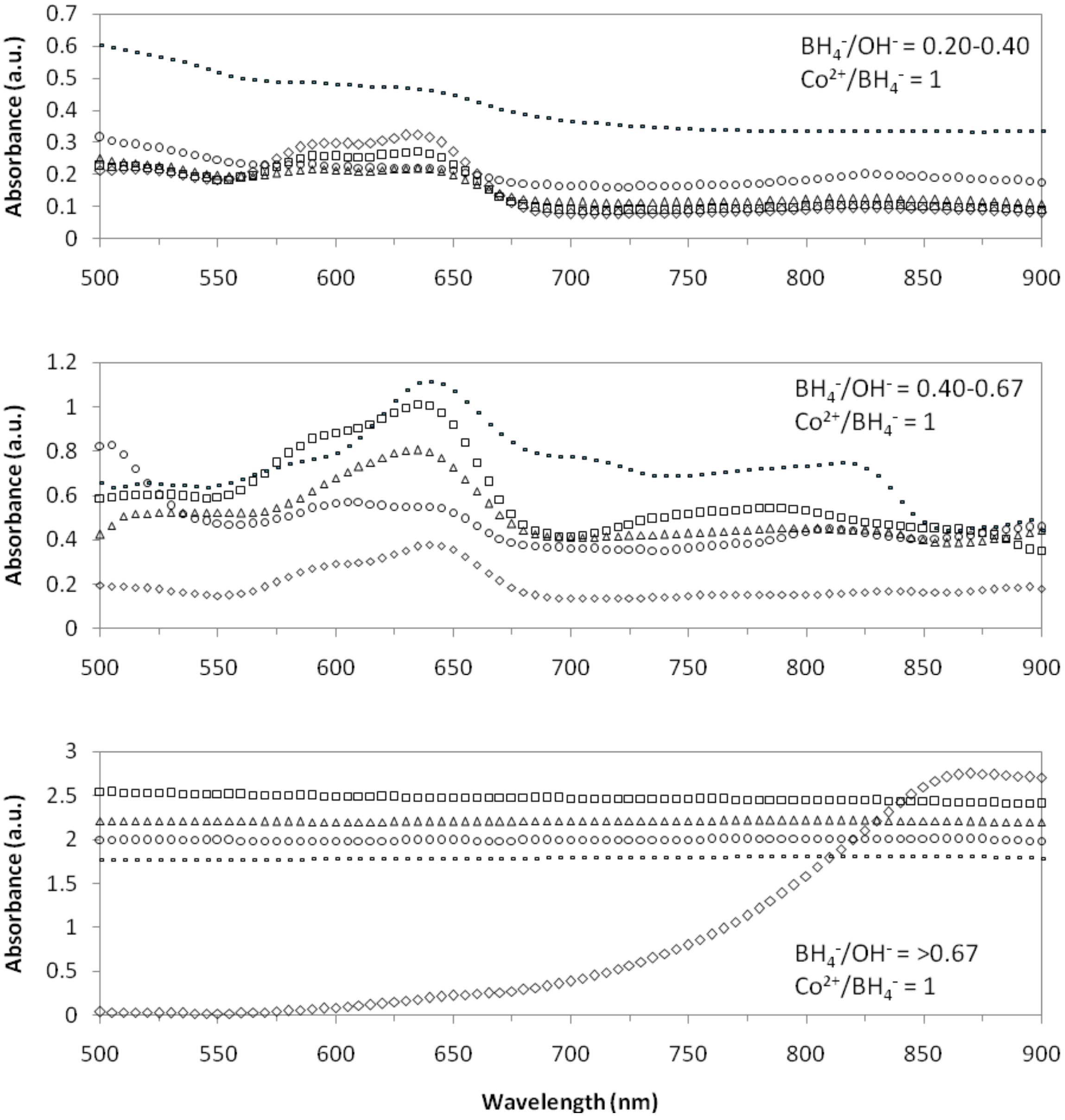

Figure S3.

Evolution of pH (top) and conductivity (bottom) when Co^{2+} is reduced by BH_4^-, Co^{2+} being from $CoCl_2$ and $Co(NO_3)_2$; with a Co^{2+}/BH_4^- ratio of 1 and BH_4^-/OH^- ratios of 0.27 (triangle), 0.5 (square) and 1 (diamond).