Ammonia borane-based reactive mixture for trapping and converting carbon dioxide

Carlos A. Castilla-Martinez[1], Bilge Coskuner Filiz[2], Eddy Petit[1], Aysel Kantürk Figen[3], And Umit B. Demirci (✉)[1]

1 Institut Europeen des Membranes (IEM), UMR 5635, Univ Montpellier, ENSCM, CNRS, Montpellier, France
2 Department of Metallurgy and Materials Engineering, Yildiz Technical University, İstanbul, Turkey
3 Department of Chemical Engineering, Yildiz Technical University, İstanbul, Turkey

E-mail: umit.demirci@umontpellier.fr

Supplementary materials

To prove the catalytic role of Pd^0, formed in situ by the reduction of $PdCl_2$ by NH_3BH_3 in our system, we performed a similar experiment without this compound. Pristine NH_3BH_3 (100 mg) was loaded in the reactor and the reactor atmosphere was filled with CO_2 (7 bar). The reactor was heated at 120 °C for 2 h. In doing so, a white powder, denoted **0**, was recovered.

0 was put in CD_3CN to be analyzed by ^1H NMR spectroscopy (Bruker Avance-400 NMR spectrometer equipped with a BBOF probe; 5-mm NMR tube). It partially dissolved. The spectrum of **0** was compared to that of unreacted NH_3BH_3 and that of the solid **1** (Fig. S1).

The ^1H NMR spectrum of NH_3BH_3 shows a triplet at about δ = 3.5 assigned to the N$\underline{H}_3$ group and a quartet centered at about δ = 1.5 that is characteristic of the B$\underline{H}_3$ group. The signal at δ = 1.9 belongs to the solvent (CD_3CN) and the intense peak at δ = 2.1 is due to the presence of residual $\underline{H}_2O$ in the deuterated solvent.

The spectrum of **0** shows the following signals. There is a singlet of medium intensity at about δ = 3.3; it likely belongs to slightly soluble thermolysis products that contain N$\underline{H}_x$ ($x \leq 2$) groups. The B-based environments B$\underline{H}_x$ ($x \leq 3$) can be seen between δ = 1.3 and δ = 0.9. There are other singlets of low/negligible intensity at about δ = 5.4 and 2.1; they are ascribed to B–N$\underline{H}_2$ groups and $\underline{H}_2O$, respectively.

The ^1H NMR spectrum of **1** shows the signals observed with **0**, as well as some others. These additional signals are as follows. There is, first, a singlet at about δ = 8.1 due to $\underline{H}COO^-$. This suggests that the in situ generated Pd^0 catalyzed the hydrogenation of CO_2 in our conditions; this confirms the positive effect of the addition of $PdCl_2$ to our system. The other singlets appear at about δ = 4.6 and between δ = 2.9 and δ = 2.7; they are likely due to O$\underline{H}$/N$\underline{H}$ bonds and C$\underline{H}_x$ groups.

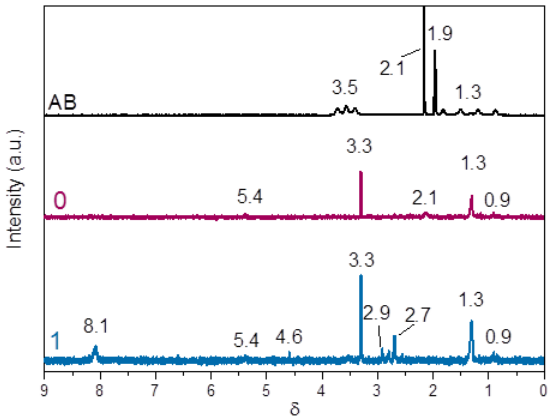

Fig. S1 ^1H NMR spectra of commercial NH_3BH_3 (unreacted), the solid **1** (obtained by reaction of CO_2 with the reactive mixture 90 wt.% NH_3BH_3–10 wt.% $PdCl_2$), and the solid **0** (obtained by reaction of CO_2 and NH_3BH_3).