SUPPLEMENTARY MATERIAL

Closing the hydrogen cycle with the couple sodium borohydride-methanol, via the formation of sodium tetramethoxyborate and sodium metaborate

Running title: Closing the hydrogen cycle with sodium borohydride-methanol

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Methanolysis of $NaBH_4$ with x = 2 equiv CH_3OH and x = 4 equiv CH_3OH

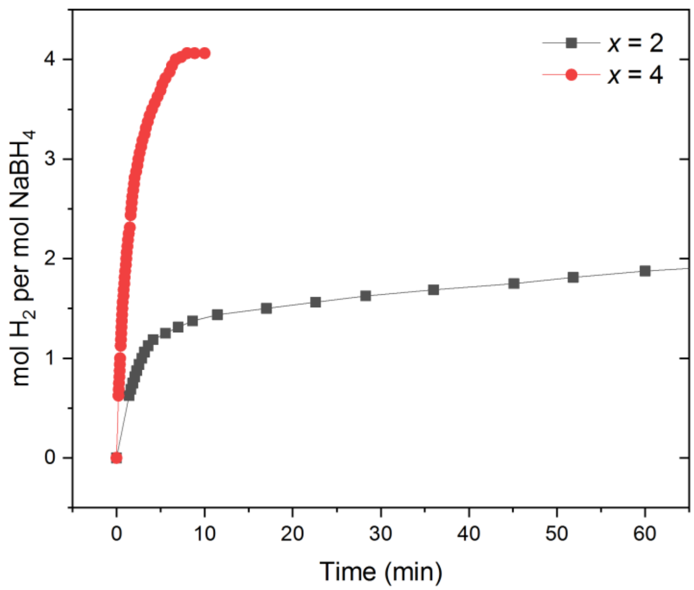

Figure S1. Hydrogen evolution curves for methanolysis of $NaBH_4$ such as x = 2 and x = 4. Because of the slow kinetics in the second part of the H_2 evolution curve with x = 2, the data collection was limited to 1 hour (and the reaction was left for completion).

SEM images of the solids recovered after methanolysis of $NaBH_4$ such as x = 2 to 32

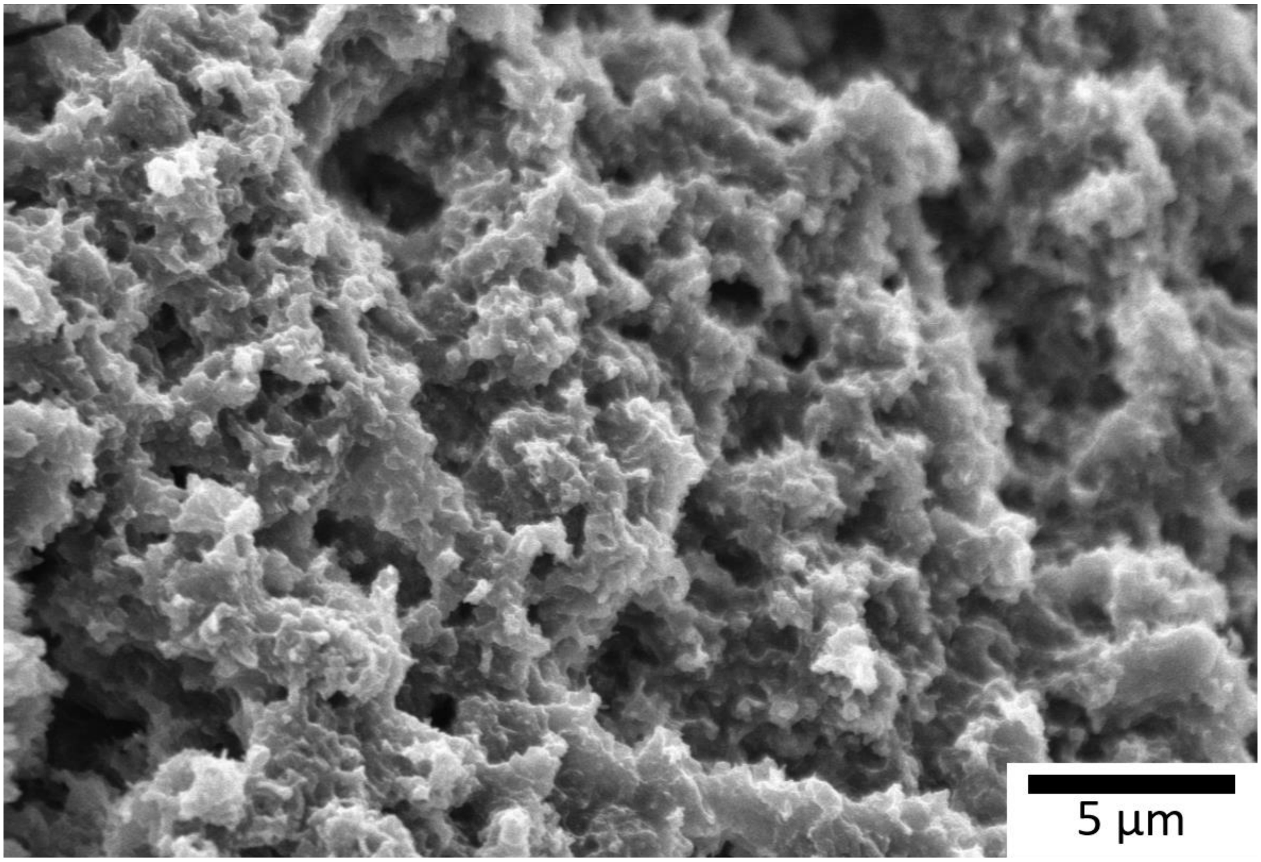

Figure S2. SEM image of the solids recovered after methanolysis of $NaBH_4$ such as x = 2.

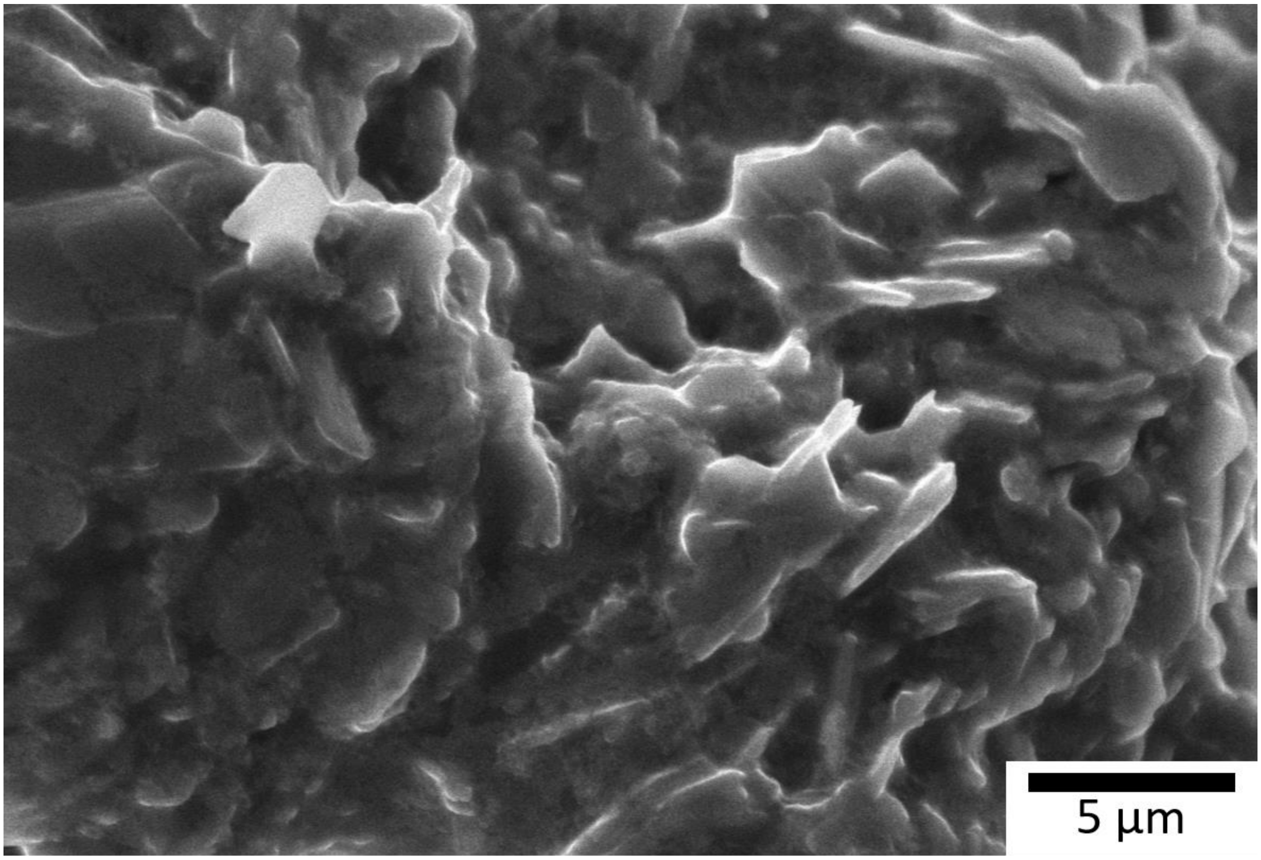

Figure S3. SEM image of the solids recovered after methanolysis of $NaBH_4$ such as x = 4.

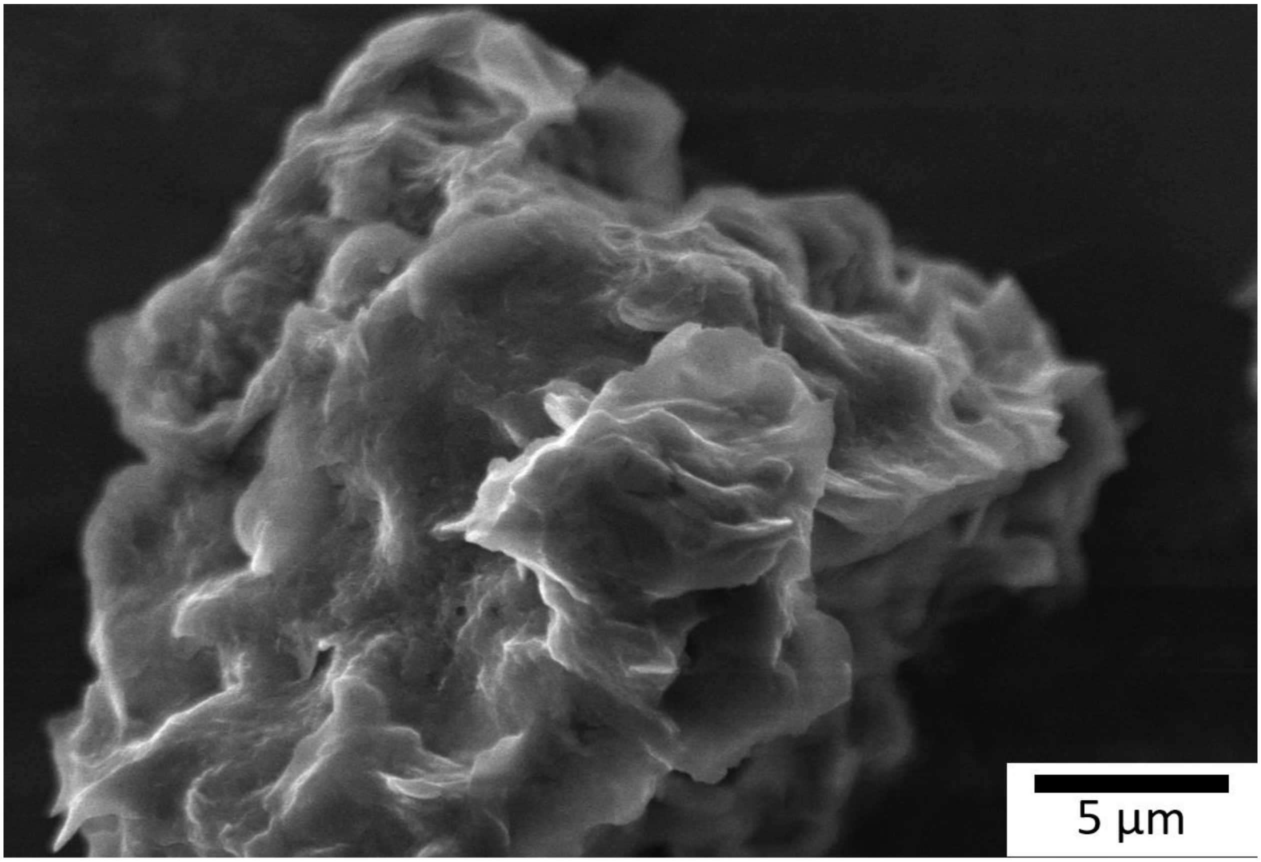

Figure S4. SEM image of the solids recovered after methanolysis of $NaBH_4$ such as x = 8.

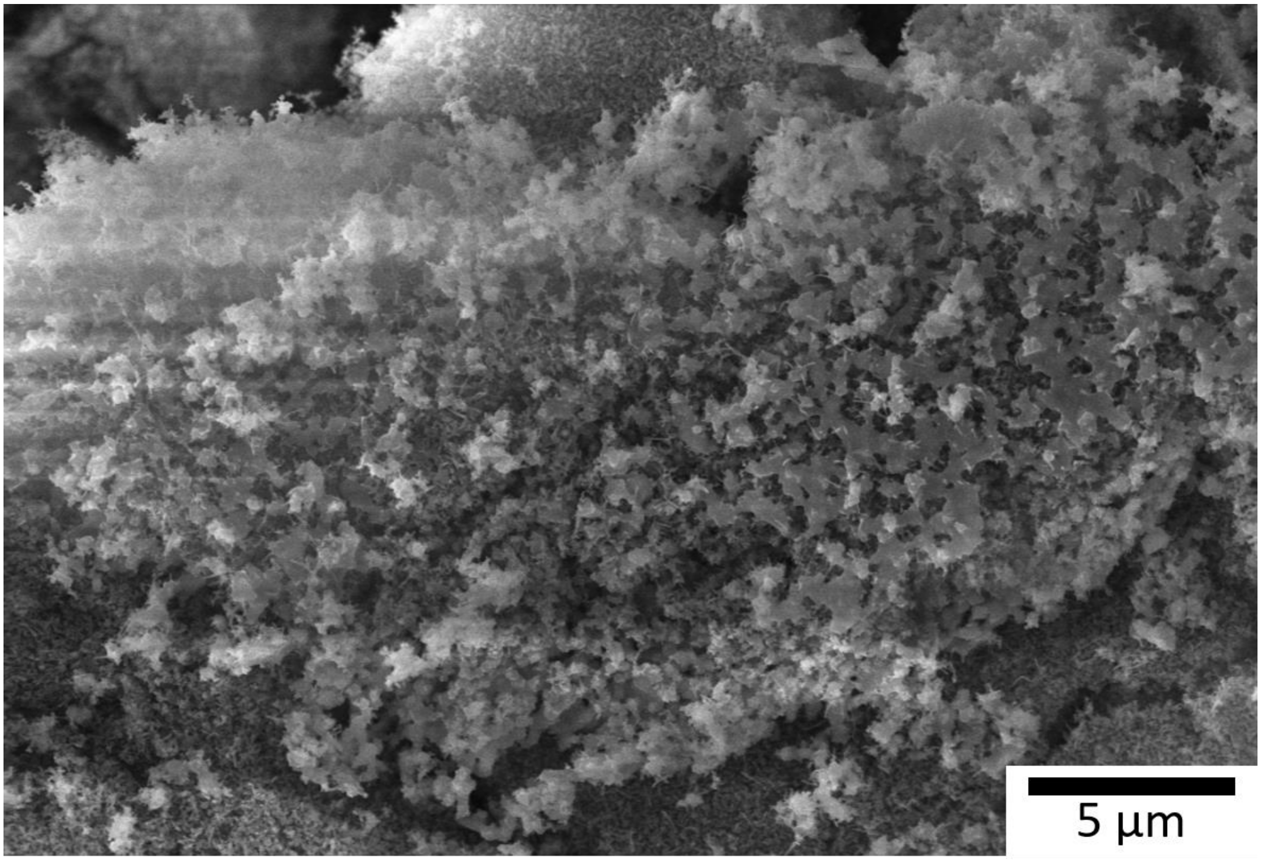

Figure S5. SEM image of the solids recovered after methanolysis of $NaBH_4$ such as x = 16.

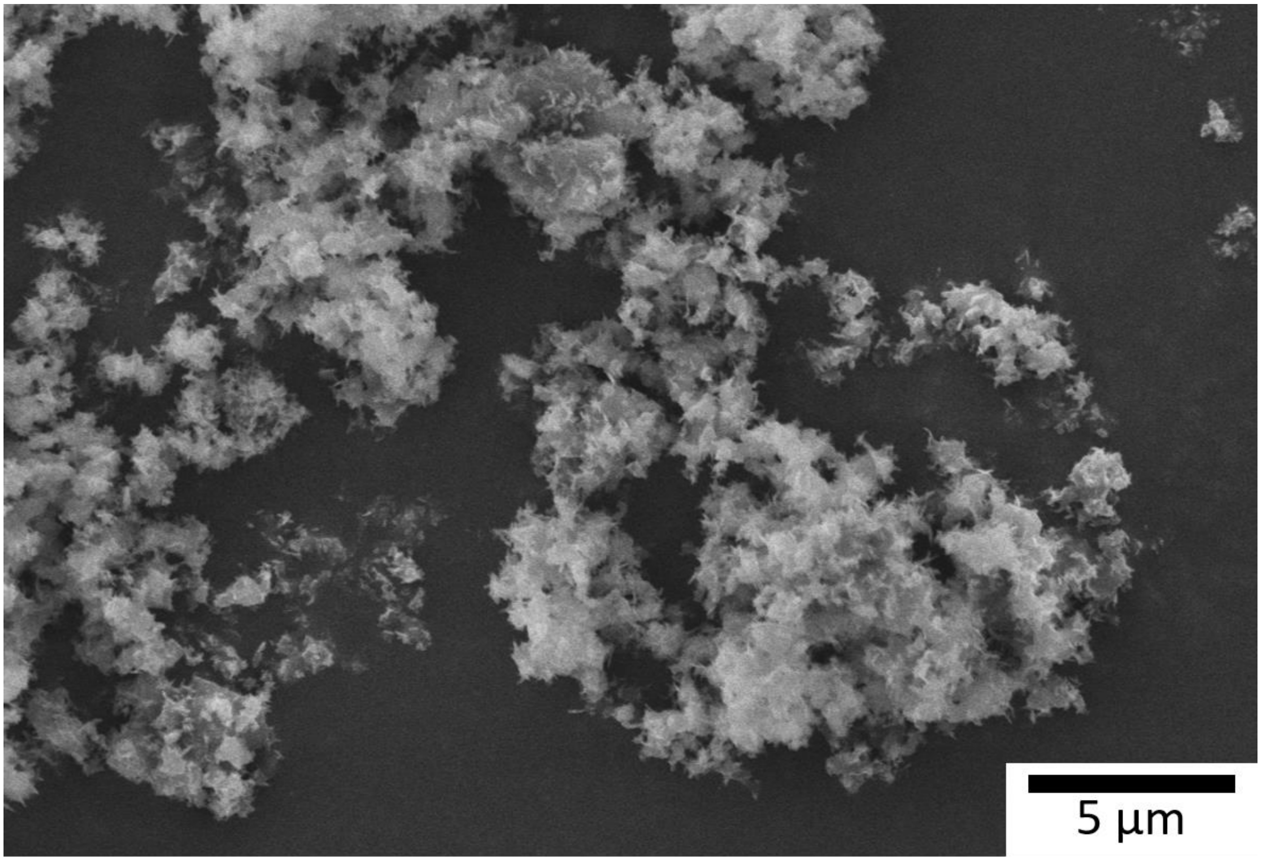

Figure S6. SEM image of the solids recovered after methanolysis of $NaBH_4$ such as x = 32.

FTIR spectra of the solids recovered after methanolysis of $NaBH_4$ such as x = 8, 16 and 32

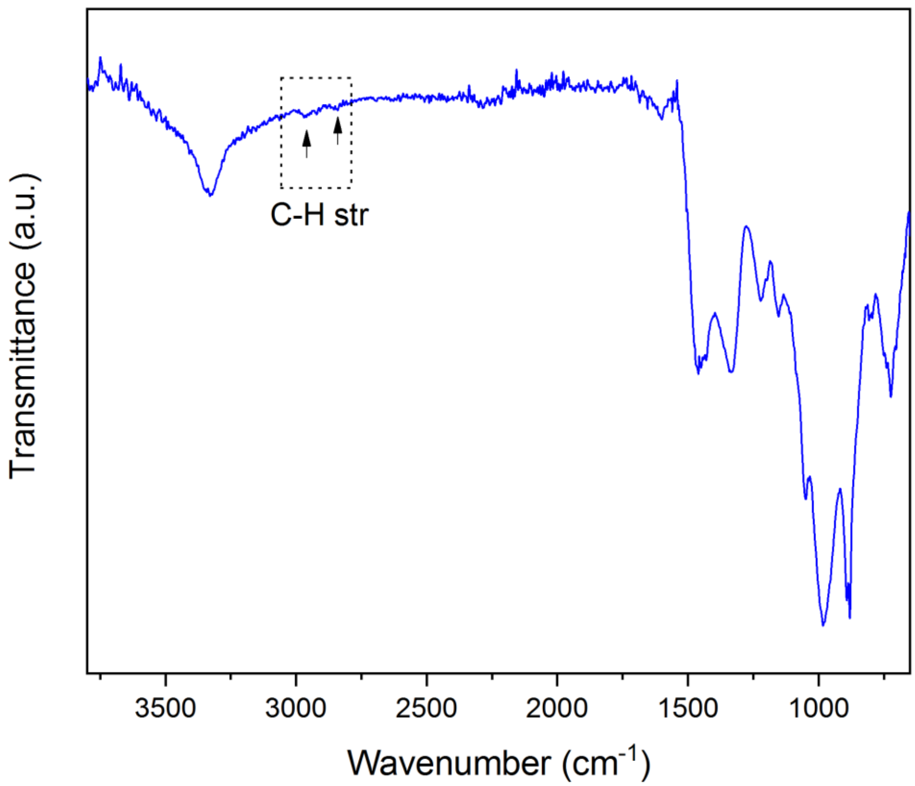

Figure S7. FTIR spectra of the solid recovered after methanolysis of $NaBH_4$ such as x = 8, to show the bands due to C–H stretching that are overlapped by the large and strong bond of O–H stretching. The other bands are ascribed in Figure 3 of the main text.

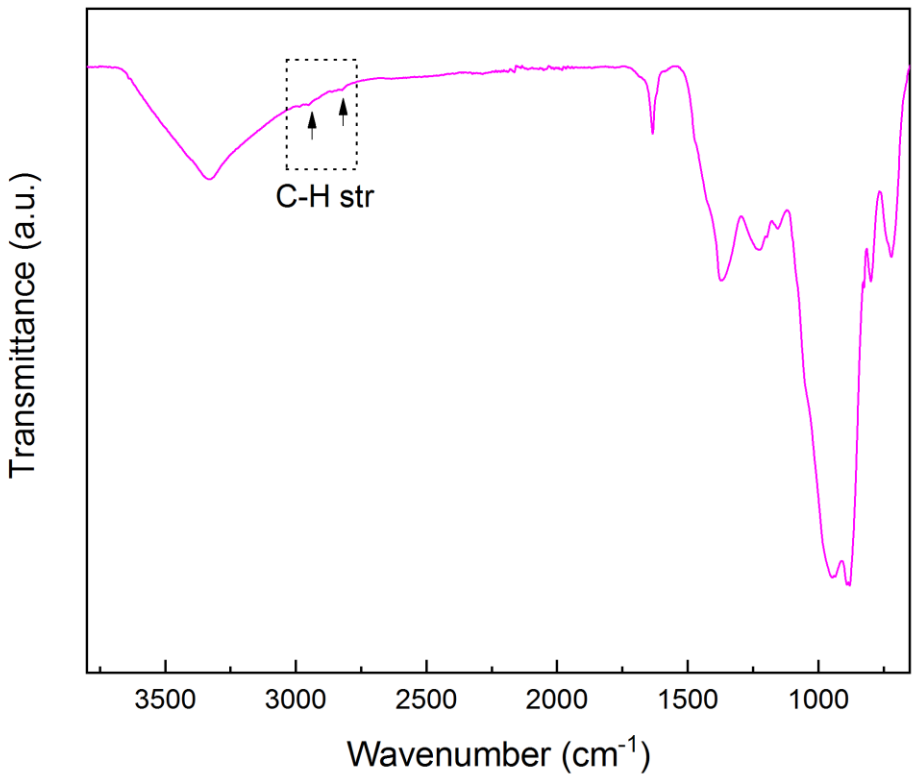

Figure S8. FTIR spectra of the solid recovered after methanolysis of $NaBH_4$ such as x = 16, to show the bands due to C–H stretching that are overlapped by the large and strong bond of O–H stretching. The other bands are ascribed in Figure 3 of the main text.

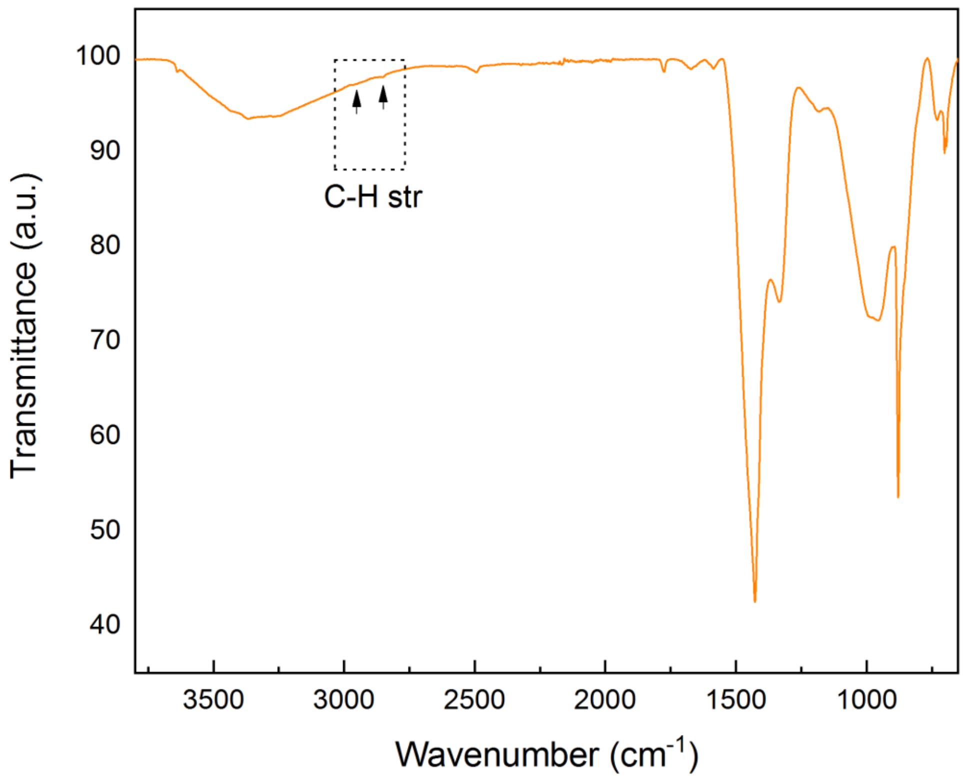

Figure S9. FTIR spectra of the solid recovered after methanolysis of $NaBH_4$ such as x = 32, to show the bands due to C–H stretching that are overlapped by the large and strong bond of O–H stretching. The other bands are ascribed in Figure 3 of the main text.

Thermal and calorimetric analysis of $NaB(OCH_3)_4$, under neutral and oxidative atmosphere

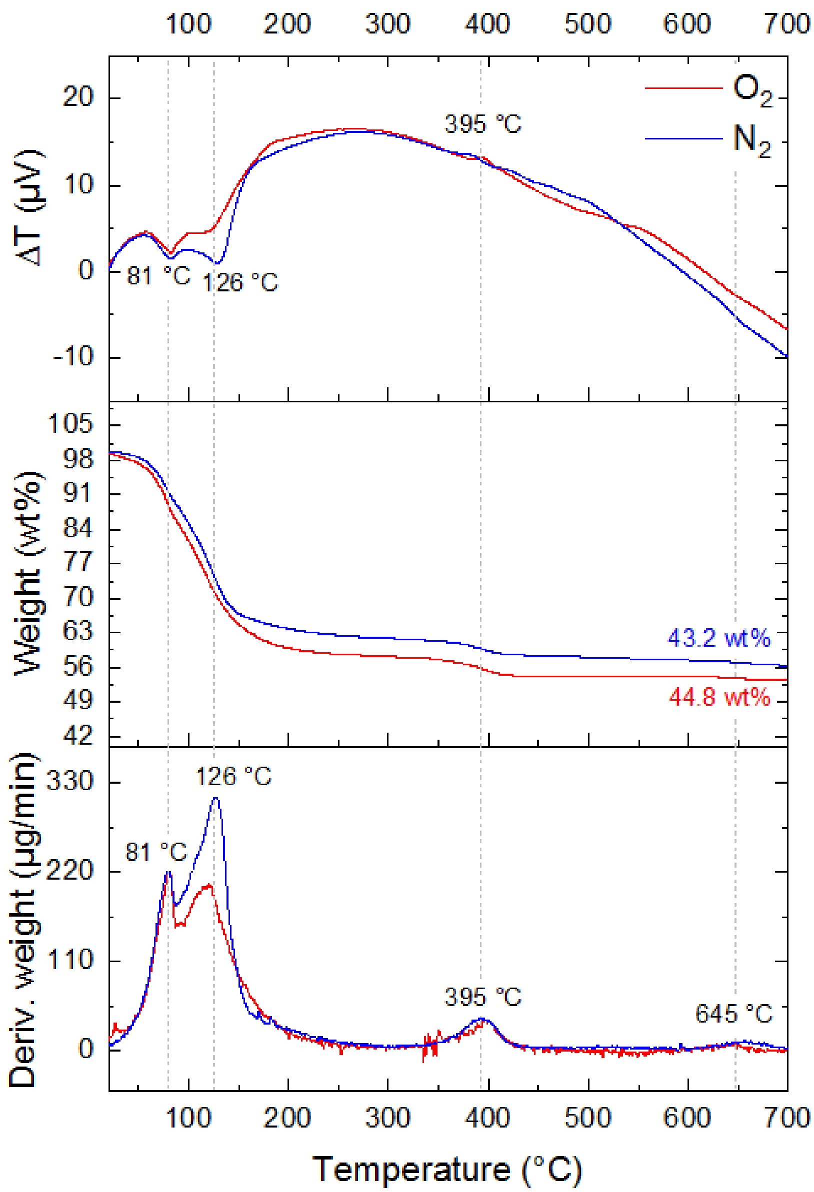

Figure S10. DTA/TG/DTG curves of the white solid obtained at *x* = 4. The experiments were performed under O_2 and N_2 atmosphere.

Analysis of the liquid phase recovered after hydrolysis of $NaB(OCH_3)_4$

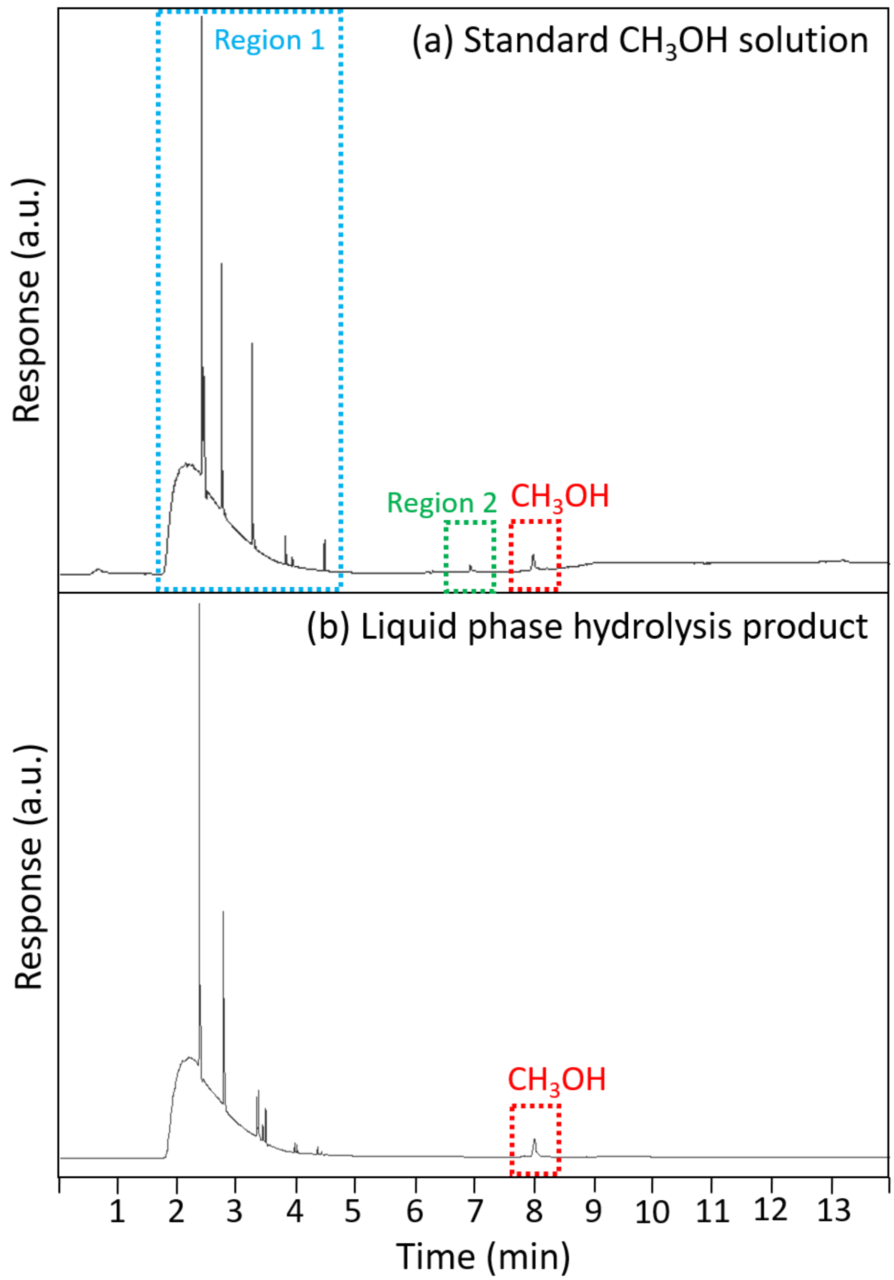

Figure S11. (a) GC-FID chromatogram of the liquid phase hydrolysis product. (b) GC-FID chromatogram of the standard CH_3OH solution. The retention time of 8 min is to that of a standard CH_3OH solution. Regions 1 and 2 are discussed hereafter.

For the GC-FID experiment, the standard solution was prepared from GC degree pure CH_3OH and deionized water as solvent. No peak from water (that does not burn) was expected because of the use of a flame ionization detector. The GC-FID chromatogram of the standard CH_3OH solution can be divided into two regions:

- **Region 1**: The peaks that are observed up to 5 min are typical of ghost peaks. They are related with the chromatograph system as reported in refs. [1,2,3].
- **Region 2**: There is one peak at about 7 min. It could be related to an impurity generally found in technical grade CH_3OH solution, as reported elsewhere [4].

The regions 1 and 2 can be seen also in the chromatogram of the liquid phase hydrolysis product (Figure S11b), thereby confirming the presence of CH_3OH.

[1] Fialkov, A.B., Steiner, U., Lehotay, S.J., Amirav, A.. Sensitivity and noise in GC–MS: Achieving low limits of detection for difficult analytes. International Journal of Mass Spectrometry 2007, 260, 31.

[2] Sparkman, O.D. GC/MS: A practical user's guide, Marvin McMaster. Journal of the American Society for Mass Spectrometry, 2008, 19(8), R1.

[3] Troubleshooting Chromatographic Contamination Ghost Peaks/Carryover, Agilent Technologies, https://www.agilent.com/cs/library/Support/Documents/a16039.pdf

[4] Lorenz, S., Bosma, M., Kemperman, A., Mohan, V., Przybytek, J., Characterization and evaluation of technical Grade dolvents and comparison to their purified counterparts. Honeywell Burdick & Jackson. Available at: http://pages2.honeywell.com/rs/honeywell2/images/Honeywell-B%26J-poster-v2b.pdf (accessed the 31st of May, 2020)