Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information

Catalyst Characterization techniques

The TEM images of the material was recorded on Philips Technai operating at 200 Kv. The powder was suspended in ethanol by ultrasonic method. A drop of this solution is placed on a grid with a holey carbon copper film and then allowed to dry, covered by a watch glass. For FTIR, all the spectra were taken at room temperature on a Horiba spectrometer FT-720. Before measurement, samples were grounded with KBr and pressed into thin wafers. XPS spectra were recorded on an Ulvac PHI 5601ci spectrometer. The pressure in the sample chamber was kept under 1 x 10^{-7} MPa The binding energy scales were adjusted to the highest C (1*s*) peak position equal to 284.2 eV. To calculate the chemical composition of the samples, empirical sensitivity factors were obtained from the relative area intensities of the photoelectron spectra of compounds of known chemical composition. Monochromatized Al $K\alpha$ X-ray (14 kV, 200 W) was used in place of a conventional X-ray source to obtain high-quality spectra to avoid overlapping of the satellite peaks; thus, uncertainty in the determinations of the peak position and peak area was nullified. An electron flood gun was used as a neutralizer, and the number of acquisitions was maintained at 12 for each analysis. To ensure the accuracy of the data, the XPS system was calibrated using the peaks of Cu (2*P*3/ 2) and Cu (3*P*) whose binding energies are 932.67 and 75.14 eV, respectively. All of the powder mineral samples were fixed onto a copper sample holder using double-sided sticky tape.

Analytical method

After separation from the solid catalyst, all products were first identified by GC-MS (Varian CP3800). Quantification of the products was obtained by a multi-point calibration curve for each product. The selectivity to each product was calculated by the following expression $S_i = C_i / \sum Cp$, where C_i is the concentration of the product 'i' and $\sum Cp$ is the total concentration of the product. Quantitative analysis was carried out using a GC (HP 6890) equipped with Innowax capillary column (Agilent, 30 m x 0.32 mm, 0.25 μm) and a flame ionization detector. The GC method used was as follows: An initial oven temperature of 50 °C was held for 3 minutes. In the next step, the temperature was ramped at 10 °C/min. until it reached 100 °C and held for 2 minutes followed by the increase in temperature to 230 °C ramped at 7.5 °C/min. and held for 20 minutes.

Method of theoretical calculation of energies

In this study, all calculations investigated by DFT were performed in accordance with the DMol3 of BIOVIA Dassault systems[1, 2]. The exchange-correlation energy function was represented by the Perdew–Burke–Ernzerhof (PBE) formalism [3]. The Kohn–Sham equation was expanded in a double numeric quality basis set (DNP) with polarization functions. The orbital cutoff range and Fermi smearing were selected as 5.0 Å and 0.001 Ha, respectively. The self-consistent-field (SCF) procedures were performed to obtain well-converged geometrical and electronic structures at a convergence criterion of 10−6 a.u. The energy, maximum force, and maximum displacement convergence were set to 10−6 Ha, 0.002 Ha/Å, and 0.005 Å, respectively.

References

1. B. Delley, *J. Chem. Phys.*, 1990, **92**, 508.

2. B. Delley, J. Chem. Phys. 2000, **113**, 7756.

3. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865.

Figure S1: A comparison of product distribution between Rh/C and Pd/C depending on the reaction time

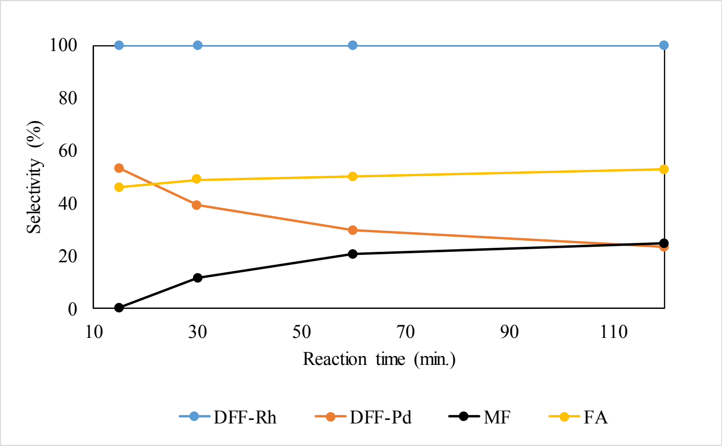


Figure S2: Phase observation of HMF in compressed CO_2 at 150 °C. (a) Empty cell, (b) HMF in the cell and (c) introduction of 8 MPa CO_2.

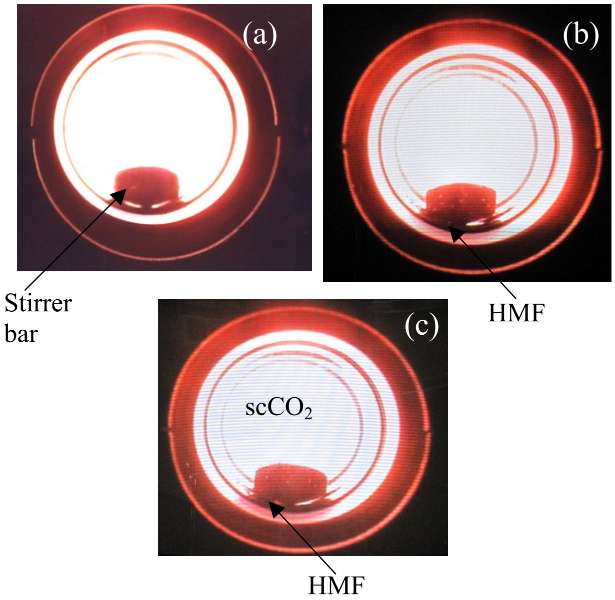
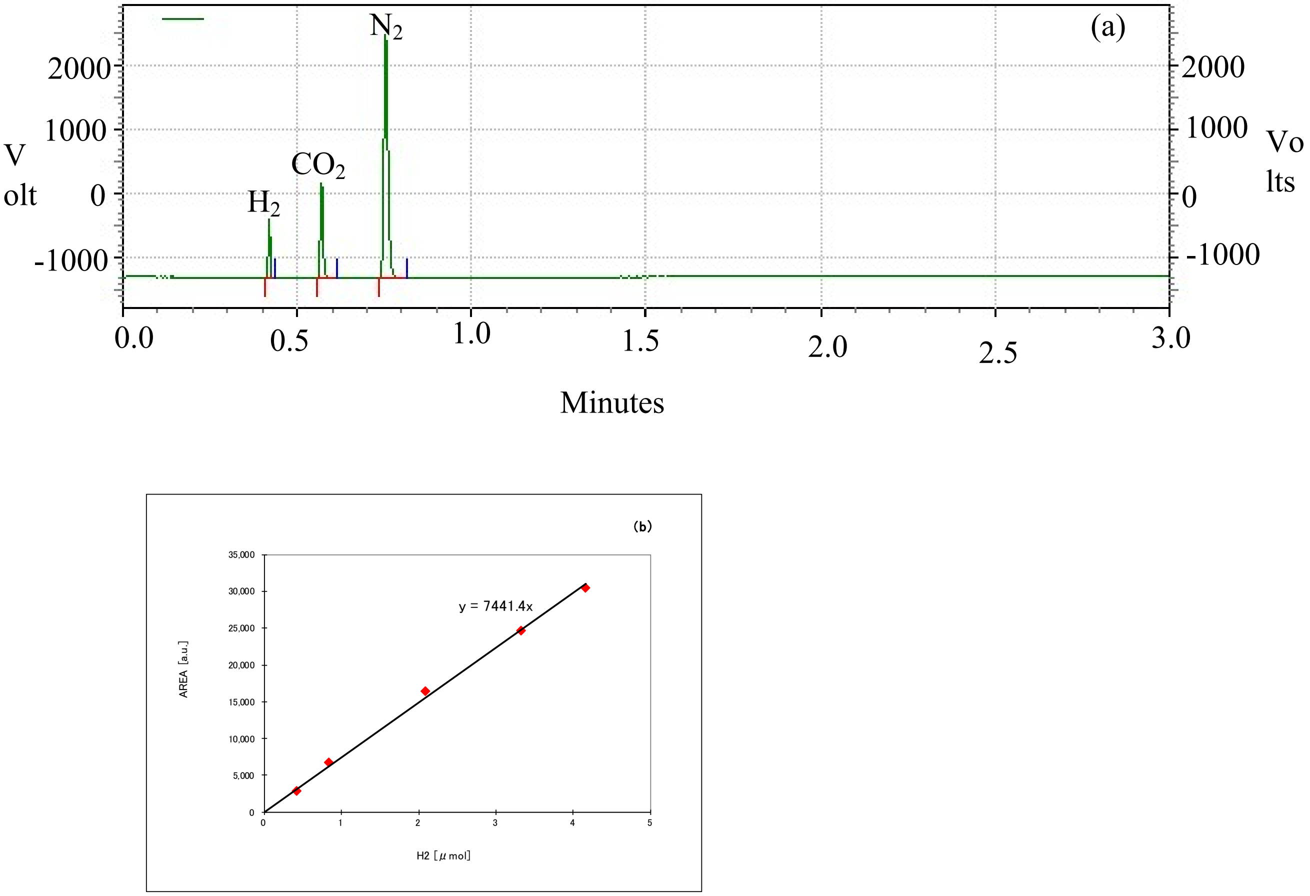


Figure S3: (a) Gas analysis chart of the liberated gas; (b) Calibration curve for quantification of hydrogen



A quantification of hydrogen was attempted using the calibration curve presented above (Figure S2 b) in the presence of a large volume of CO_2, which was a challenging task and we are unable to fully guarantee the accuracy of the selective trapping of the hydrogen gas. A possible quantification of hydrogen was revealed a best qualitative guess of ~ 15 % for the reaction at 150 ºC, reaction time= 2 h; P_{CO2}= 8 MPa using Rh/C catalyst.

Figure S4: TEM images of Rh/C (a) before and (b) after reaction

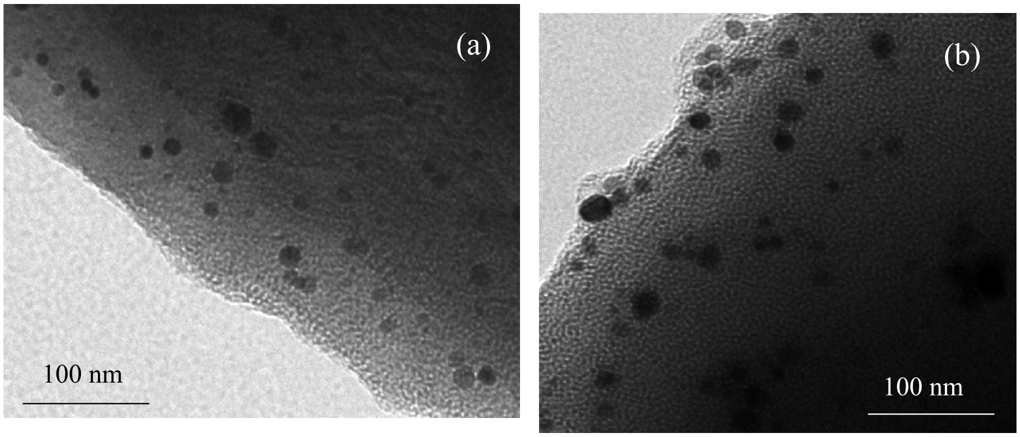


Figure S5: FTIR spectra in the region of 1800- 1000 cm^{-1} of (a) used catalyst and (b) HMF