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Supporting Information

Insights on Hydrogen Spillover on Carbonaceous Supports

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1. Gas chromatography (GC) analysis

Gas chromatography (GC): After each sample was hydrogenated to the desired level, an aliquot of 11 ± 1 mg of the sample was mixed with 8.5-9.0 ml of toluene and stirred for 1 hour at room temperature, in order to dissolve all organic compounds. The suspension was filtered into a 10 ml volumetric flask. Then, 1 ml of triphenylphosphine oxide (Ph_3PO, 2 g/L) solution in toluene was added as an internal standard, and the remaining volume was filled to 10 ml with toluene. The distribution of PEB hydrogenation products was analyzed on a Hewlett Packard 5890 gas chromatograph equipped with a flame ionization detector and SGE BP1 capillary column (cat. No. 054062; 30 m length, 0.32 mm internal diameter, with 0.25 μm film of 100% polydimethylsiloxane), using helium as a carrier gas. The temperature program is shown in Figure S1. Each sample solution was injected four times. Identification of the products was done by mass spectrometry, as previously reported [**Error! Reference source not found.**]. The quantitative analysis was performed according to calibration curves.

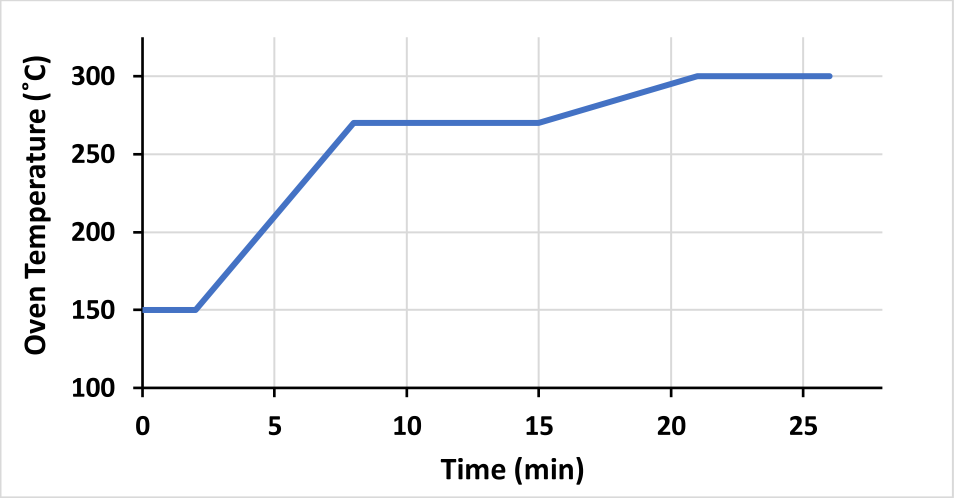

Figure S1. The gas chromatography column temperature program. The temperatures of the GC injector and detector were 270 and 300 °C respectively.

2. An exothermic effect

The kinetic measurements for the PEB hydrogenation are presented in Figure 1 of the main text.

As shown, the initial H_2 pressure influences the rate of the reaction progress.

This is true not only in the aspect of hydrogen availability, but also as a result of the differences in the reaction temperature, due to the exothermic nature of the hydrogenation reaction. The temperature of the reaction mixture was measured *in-situ* during hydrogenation and was found to reach up to 150 °C, well below the PEB melting point (182 °C).

The exothermic effect could be clearly deduced by the below analysis as well:

For each dose, the hydrogen pressure drop is measured. A dose with an initial hydrogen pressure of 100 torr decreases to 2 torr before another hydrogen dose is inserted; and for a dose with an initial pressure of 20 torr, the pressure decreases to 0.4 torr respectively (Section 2.3 of the main text). Thus, the common pressure range, over which the reaction advances in both sets of hydrogenation conditions, is between 20 and 2 torr. When comparing the time it takes for the hydrogen pressure to drop from 20 to 2 torr, one may note (see Figure S2) that these times are much shorter for the samples hydrogenated at a higher initial pressure. This is observed throughout the entire course of the reaction progress, but most evidently at the beginning.

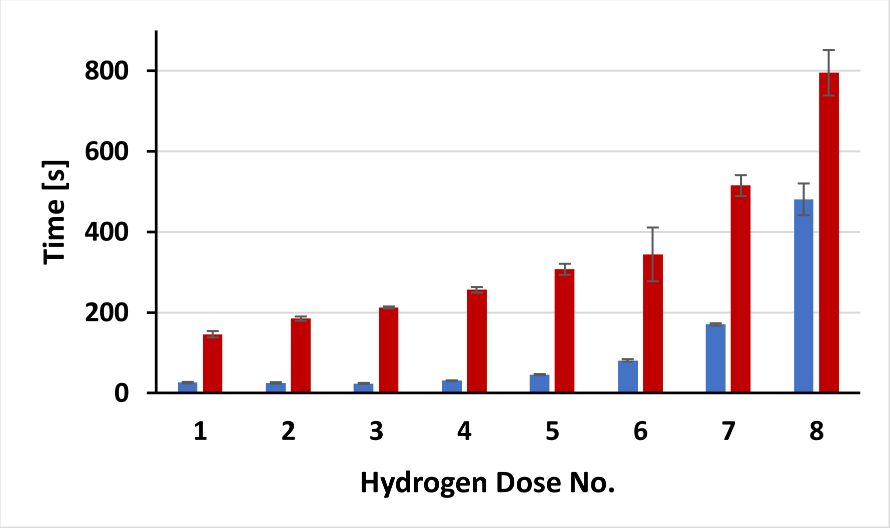

Figure S2. Times of H_2 pressure drop between 20 torr and 2 torr for samples hydrogenated with an initial H_2 pressure of 100 torr (blue) and 20 torr (red).

From this observation, we can conclude that at higher initial pressures, the heat that is released during the hydrogenation significantly influences the reaction rate. While the same amount of heat per mole is released at the lower initial pressure, it is released over an extended time in a non-adiabatic system allowing for heat dissipation and consequently, leads to a smaller temperature increase, which in turn causes slower reaction rate.

3. Hydrogenation Products Distribution

In the main text, the products distribution in the samples after hydrogenation reaction is presented throughout the reaction progress. Figure 3 presents a summarized view showing all partially hydrogenated products as one. A more detailed view is presented below (Figures S3a-S3f) for all the studied reaction conditions and compositions.

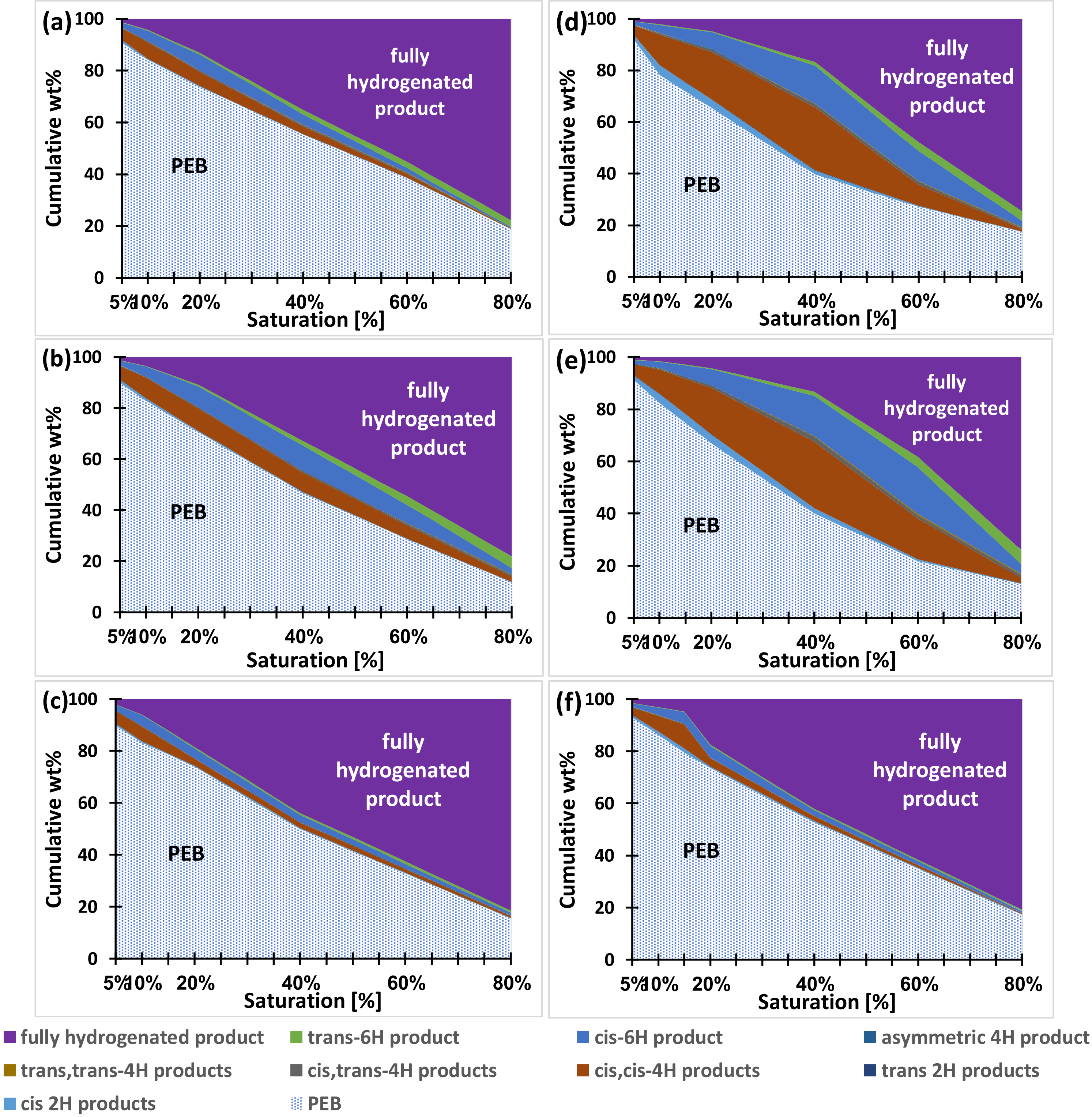

Figure S3. The relative amounts of PEB hydrogenation products as a function of the reaction progress for experiments performed at an initial H_2 pressure of 20 torr (a) without additives, (b) with CNTs, (c) with C_{60}; and 100 torr (d) without additives, (e) with CNTs, (f) with C_{60}.

4. Addition of C_{60}-fullerenes

Addition of C_{60} to the reaction system had a severely decelerating influence on the reaction rate. This seems to be independent on the quantity of C_{60} that was added, at least in the range 5-10 wt%, as the addition of 5 and 10 wt% of C_{60} fullerene have a comparable effect on the reaction kinetics. Similar effect was observed even when both C_{60} and CNT were added (Figure S4).

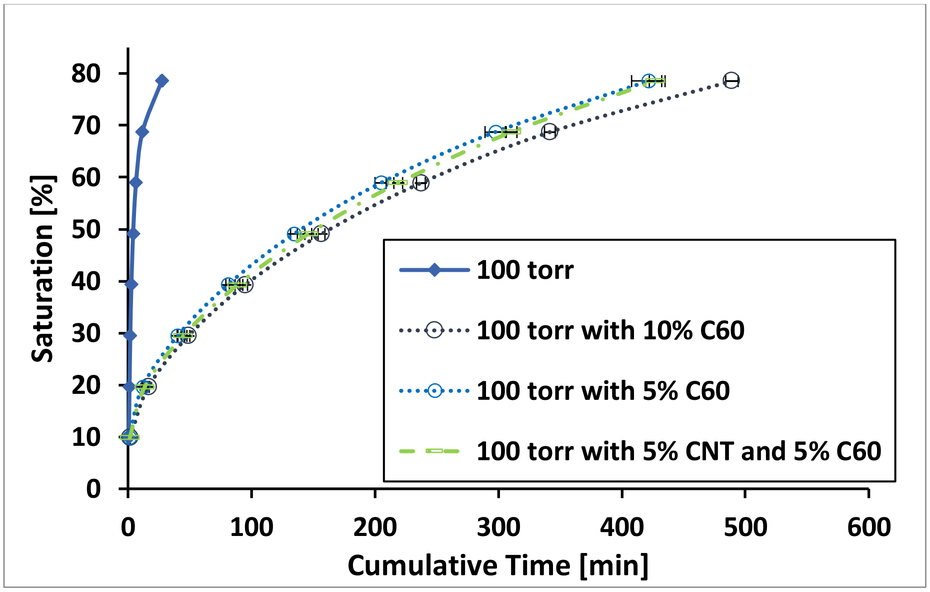

Figure S4. The progress of PEB hydrogenation over time with an initial hydrogen pressure of 100 torr, and with the addition of 5 and 10 wt% of C_{60} fullerene, with and without CNTs.

5. Cis/trans Hydrogenation Products Ratio

As can be observed in Figures S5a-S5d, there is a high kinetic preference towards the cis- partially-hydrogenated products. In all the systems that were studied, the cis/trans ratio was initially high and decreased with the reaction progress (Figure S5). This is an indication that while the *syn*- addition is kinetically favored, the thermodynamically stable trans- product is less reactive than the *cis*- product.

Another insight may be deduced from the shape of the curves of the cis/trans ratio through the reaction progress (Figure S5). For the lower hydrogenation pressure, where the availability of the active H-atom is relatively low, the cis/trans ratio drops faster than for the higher hydrogenation pressure. The addition of CNTs has little to no effect on the curvature since it does not affect the H-atoms availability (Figure S5a). The CNTs only help the migration of the H-atoms and do not affect the rate of H_2 molecules dissociation and transfer to the solid phase. At the lower H_2 pressure (20 torr) the curves with and without CNTs have a similar shape but do not overlap. This is due to an initial increase of the cis/trans ratio for the system with CNTs, caused by the broader hydrogen dispersion in the system that contains CNTs. On the other hand, the addition of C_{60} gives the cis/trans ratio a curvature characteristic of the lower hydrogenation pressure (dotted lines, Figure S5b), indicating a decrease in H-atom availability. It can be concluded that the C_{60} removes the adsorbed H-atoms from the support or inhibits its formation.

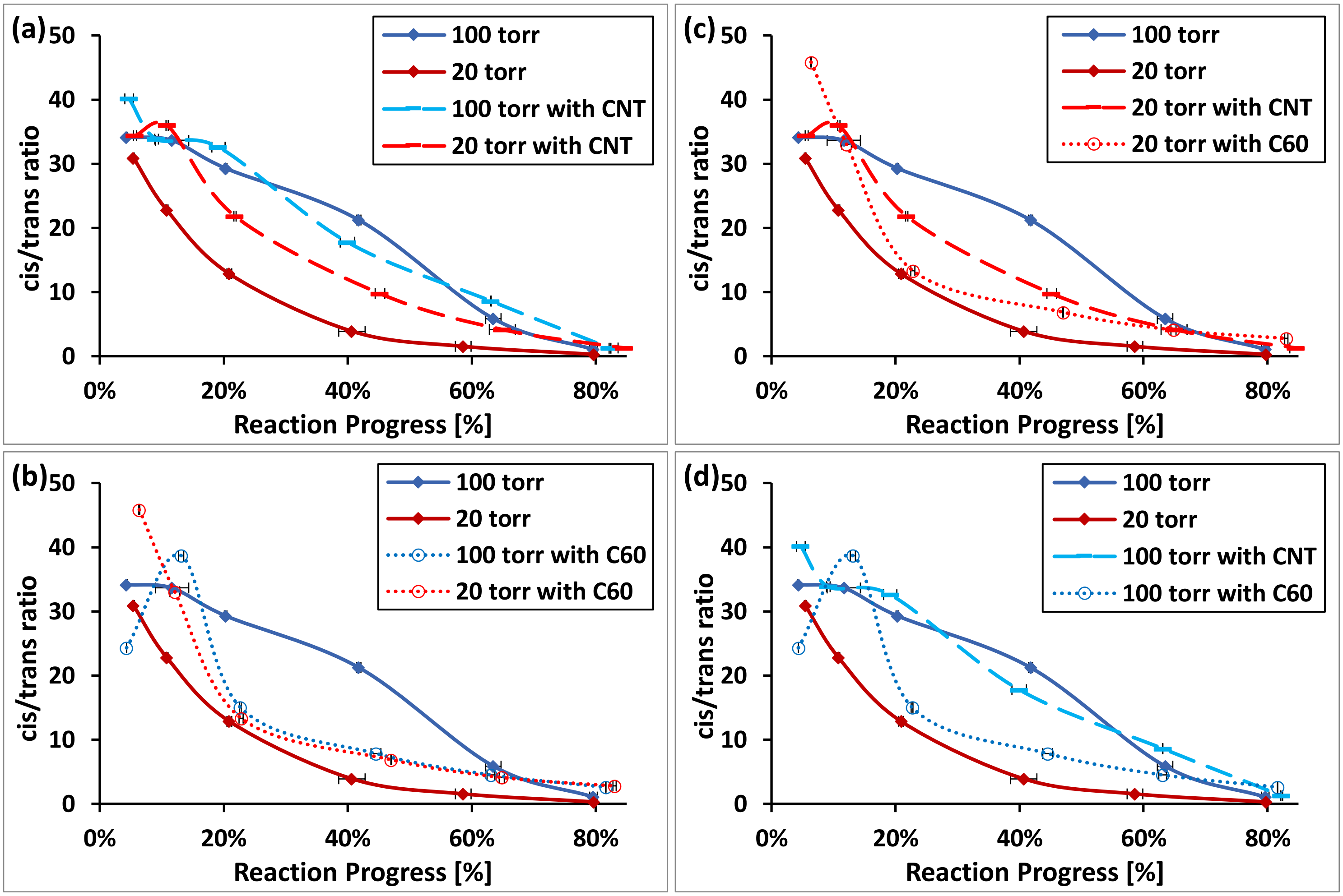

Figure S5. The cis/trans ratio of the hydrogenation products of PEB as a function of the reaction progress: (a) with and without carbon nanotubes at both hydrogen pressures; (b) with and without C_{60} at both hydrogen pressures; (c) compared effect of CNTs and C_{60} at a pressure of 20 torr; (d) compared effect of CNTs and C_{60} at a pressure of 100 torr.