Cyclohexene Epoxidation with Cyclohexyl Hydroperoxide: A Catalytic Route to Largely Increase Oxygenate Yield from Cyclohexane Oxidation

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Supporting information

I. Additional catalytic data

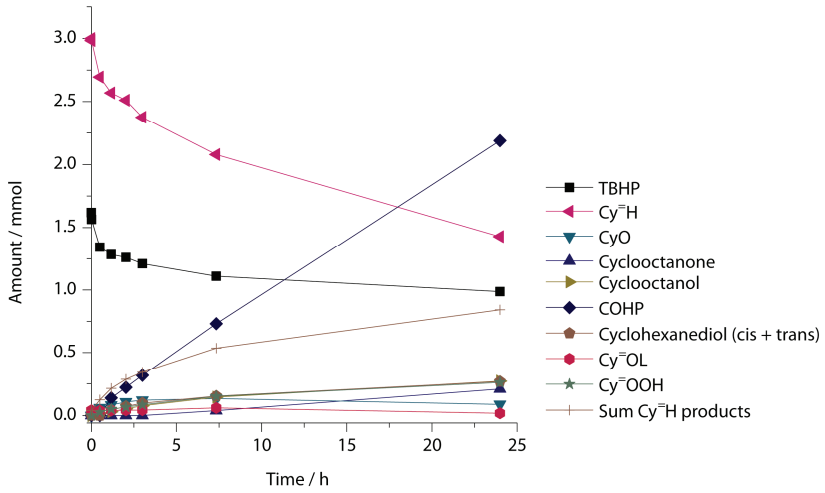

Figure S1. Amounts of the different species present in the reactor in mmol during cyclohexene epoxidation with TBHP over Ti-G40-SBA at 80°C.

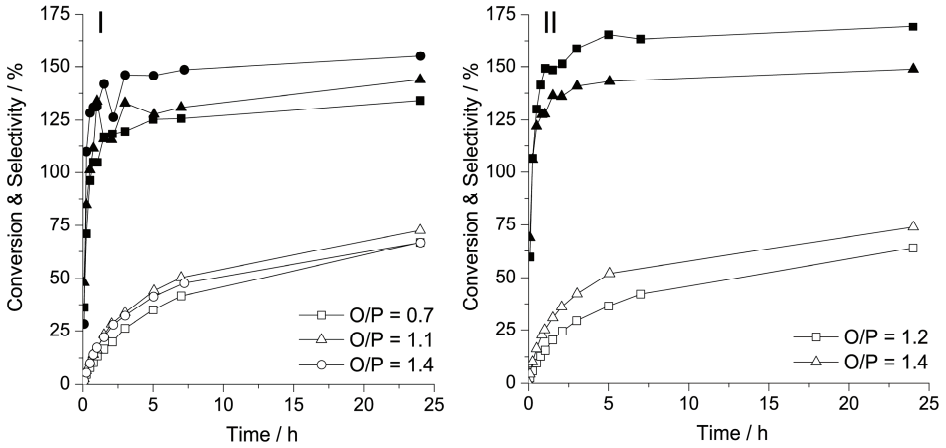

Figure S2. Influence of the applied O/P ratio on the catalytic performance of Ti-G80-SBA (I) and Ti-G40-SBA (II).

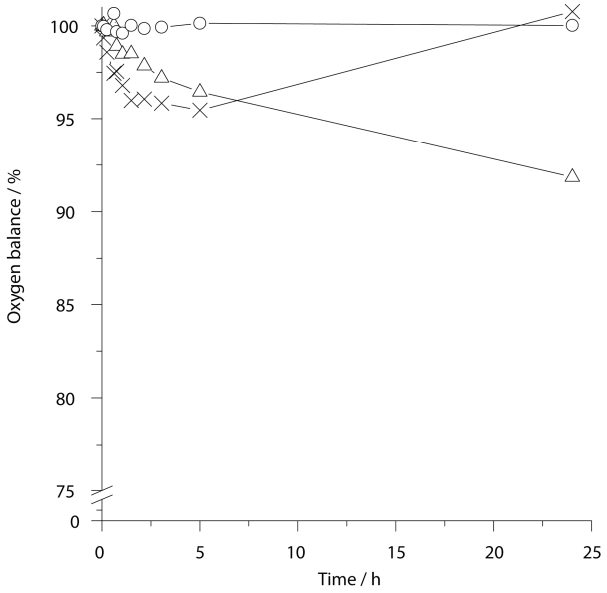

Figure S3. Oxygen balance (X), oxygen selectivity with (□) and without (○) water formation taken into account during the epoxidation reaction over Ti-G80-SBAp900 catalyst material at 80°C. The applied O/P ratio was 1.4.

II. Cyclohexene balance

As already stated, the cyclohexene oxide selectivity based on the cyclohexene conversion lay between 60 and 80 % at 5 h on stream for all different experiments. Since the other products that evidently originate from cyclohexene *i.e.* the unsaturated alcohol, ketone and hydroperoxide and 1,2-cyclohexanediol, only account for a small percentage of the cyclohexene conversion, an amount of cyclohexene cannot yet be traced back. A series of reference experiments has been conducted to unravel the cause of incomplete cyclohexene balance. These considerations will be discussed here.

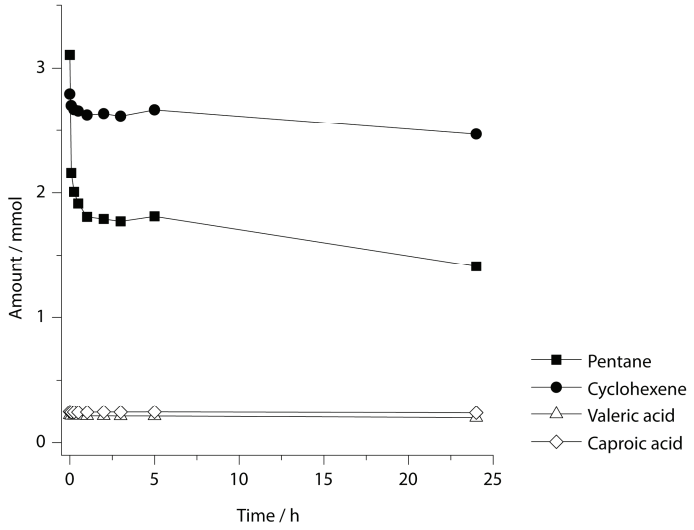

Figure S4. Evaporation experiment. A mixture of cyclohexene, pentane, valeric acid and caproic acid in cyclohexane was stirred for 24 h at 80°C in the presence of 50 mg Ti-G40-SBA.

In order to investigate the possibility of cyclohexene evaporation from the reactor, several experiments were conducted. At first, performing a reaction in a flask without septum and with double amount of reactants and solvent and no sample extraction during the experiments yielded:

- $Cy^{=}H$ balance of 55 %,
- Mass balance of 99.7 % (based on the mass of the flask before and after reaction)
- Oxygen selectivity 86 % (99 % when the estimated water formation is left from the calculation)

$$\text{Oxygen Selectivity} = \frac{\#\text{ mole oxygen in cyclic molecules}}{\text{total }\#\text{ mole oxygen in all oxygenates}} * 100\%$$

Although the missing $Cy^{=}H$ (0.14 g) accounts only for 0.15 % of the total mass, assuming a similar evaporation rate for cyclohexene and cyclohexane (based on the similar boiling points of 83°C and 80°C) and given the low concentration of $Cy^{=}H$, a significant amount of cyclohexane should have evaporated as well, which would have let to a significant

decrease of the total mass of 8 g or 8.5 % of the total mass. Thus in this case evaporation loss of cyclohexene seems not to be the case.

In Figure S4, the results of an experiment studying possible evaporation effects during sampling are presented. A mixture of Cy⁼H, valeric and caproic acid and pentane as a volatile inert species were stirred for 24 h at 80°C. It was observed that the amounts of pentane and cyclohexene in the reaction mixture follow a comparable trend. Since the pentane amount decreased much faster, these results are a strong indication of evaporation problems, most probably caused by leakage of the septum when withdrawing samples. However, the loss of 11 % Cy⁼H in this case does not explain the total amount of missing Cy⁼H after an epoxidation reaction, which is in in the order of ~ 1 mmol or 40%.

A second experiment involved the epoxidation of cyclododecene with CyOOH in the presence of an initial amount of ~ 1 mmol CyO of which the results are displayed in Figure S5. It was observed that the amount CyO present decreased as well over time, while this could not be explained by the formation of significant cyclohexanediol, or other (unidentified) peaks of significant size appearing in the chromatograms. Cyclohexene oxide might polymerize in the presence of radicals and thus disappear from the reaction mixture. That way, also an incomplete cyclohexene balance is obtained. However, taking into account the high CyO selectivity based on CyOOH conversion and the high oxygen balance as is shown in Figure S3, this also cannot explain the whole amount of missing Cy⁼H. Additionally, in a real epoxidation experiment, the starting concentration of CyO is zero, thus the effect of CyO conversion has to be much smaller in the first hours of reaction leading to a lower final CyO conversion as well. Nevertheless loss of cyclohexene due to CyO conversion is a plausible scenario.

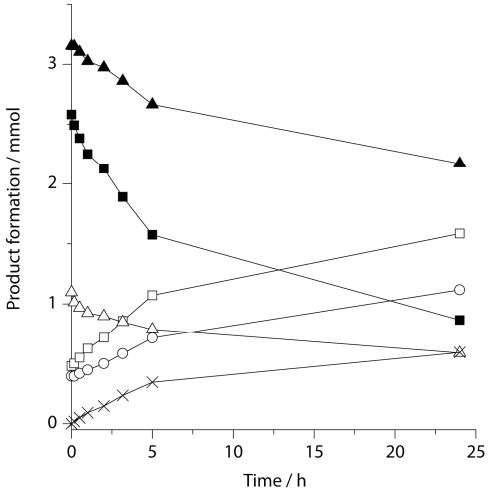

Figure S5. Molar reactor content during cyclododecene epoxidation over Ti-G40-SBA at 80°C and applied O/P ratio of 1.2. CyOOH (■), Cy⁼H (▲), CyOH (□), Cy=O (○), CyO (△) and cyclododecene oxide (×). The FID response factor for cyclododecene oxide with respect to biphenyl was estimated.

In a final experiment, a mixture of CyOOH and Cy$^{=}$H in CyH plus additional CyO was heated for 24 h without a catalyst present in a flask without septum. In this case only thermal decomposition of the peroxides has to be expected and evaporation is excluded. 70 % of the cyclohexene could be traced back to products (Table S1). Since in this case the amount of CyO remained constant, we can conclude that CyO might be converted only when a catalyst is present. However, still some Cy$^{=}$H cannot be traced back to products, which might be caused by radical propagation reactions. The occurrence of radical attack on cyclohexene is evidenced by the presence on allylic oxidation products in the reaction mixture.[47, 48] Radical propagation reactions of Cy$^{=}$OOH might cause decomposition of some of the cyclohexene.

Table S1. Molar amount of reactants and products present in the reactor before and after stirring an epoxidation starting mixture without catalyst for 24 h at 80°C.

Species	**Start amount (mmol)**	**24 h amount (mmol)**
CyOOH	2.57	2.45
CyOH	0.48	0.65
Cy=O	0.40	0.57
Cy$^{=}$H	3.33	2.54
CyO	1.19	1.26
Cy$^{=}$OOH	0.11	0.49
Cy$^{=}$OH	0	0.04
Cy$^{=}$One	0	0.07