

Electronic Supplementary Information

Method: Hydrogenolysis/Hydrogenation of aryl ether compounds

The reaction was conducted in a 50 ml batch reactor containing catalyst, substrate (wt ratio of catalyst: substrate = 1: 5) and water placed in an oven with fan heater to maintain the constant temperature. After reaching the desired temperature, hydrogen of required pressure was first introduced into the reactor. Liquid CO₂ was charged into the reactor using a high pressure liquid pump (JASCO). The reaction mixture was stirred continuously with a teflon coated magnetic bar during the reaction. After the reaction, the reactor was cooled by ice-water and depressurized carefully by the back-pressure regulator. The aqueous and the organic part were separated from the catalyst simply by filtration. The product mixture was identified and quantitatively analyzed by GC/MS (Varian Saturn 2200). 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 $S_i = C_i / \sum C_p$, where C_i is the concentration of the product 'i' and $\sum C_p$ is the total concentration of the product.

Phase change observations

Method: Visual observation of phase behaviour of diphenyl ether (DPE) in scCO₂ under the studied reaction condition was conducted separately using a 10 ml high pressure view cell fitted with a sapphire window. The cell was placed over a magnetic stirrer for stirring the content and connected to a pressure controller, to regulate the pressure inside the view cell. In addition, temperature controller was used to maintain the desired temperature of 80 °C. In the beginning, DPE was introduced into the view cell at a constant H₂ pressure of 0.5 MPa while CO₂ pressure was varied in the range of 7-16 MPa and the phase change was shown in ESI Figure 1.

ESI Figure 1: Phase change observations of DPE at 80 °C and $P_{H_2} = 0.5$ MPa: (a) 10 MPa and (b) 16 MPa

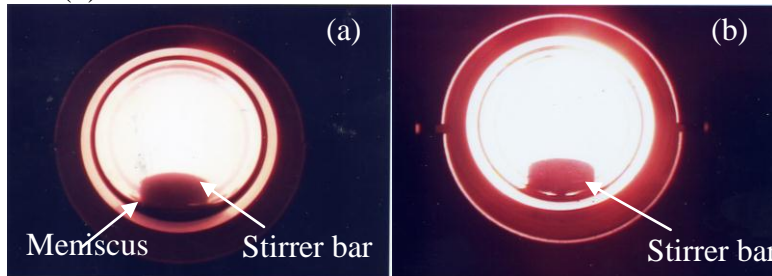
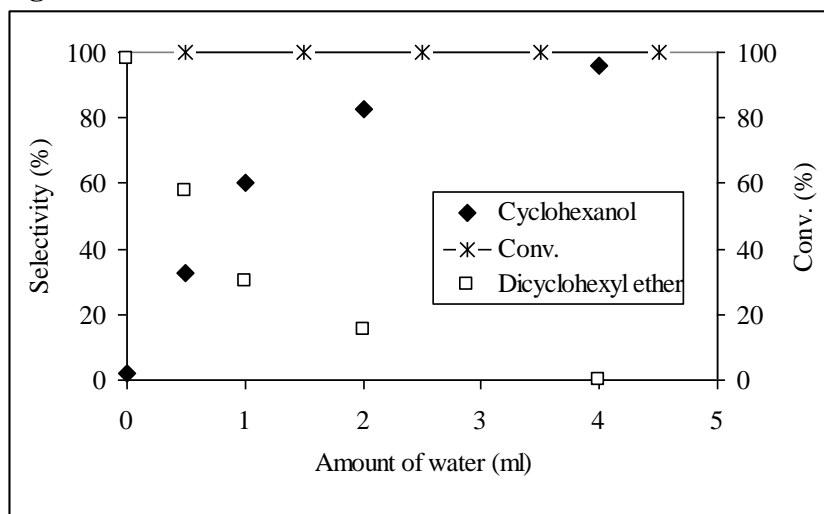


Figure 2: Variation of the amount of water



Reaction condition: catalyst: substrate = 1: 5, temperature= 80°C, reaction time = 5h, $P_{H_2} = 0.5$ MPa, $P_{CO_2} = 10$ MPa

ESI Table 1: Combined effect of different organic solvent and water in DPE hydrogenolysis/hydrogenation

Entry	Solvent	Conv. (%)	Product selectivity (%)			
			DCHE	CHPE	CHOH	CH
1	Water only	14.8	68.0	0.0	22.5	9.5
2	Methanol/water	47.6	13.2	11.5	58.9	16.4
3	Ethanol/water	60.2	2.4	0.0	84.2	13.4
4	Isopropanol/water	85.6	0.0	6.8	92.0	1.2
5	Tetrahydrofuran/water	92.1	57.3	0.0	37.6	5.1
6	Hexane/water	100.0	70.3	0.0	27.7	2.3
7	scCO ₂ /water	100	0.0	0.0	96.0	2.2
8	scCO ₂ /water	94.5	0.0	0.0	97.2	1.8

Reaction condition: catalyst: substrate = 1: 5, temperature= 80°C, reaction time = 5h, amount of water= 4 ml, $P_{H_2} = 0.5$ MPa, solvent= 5 ml; DCHE= dicyclohexyl ether, CHPE= cyclohexylphenyl ether, CHOH= cyclohexanol, CH= cyclohexane; Entry 7 and 8= results after 1st and 5th recycling of the catalyst.