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Palladium catalysts based on porous aromatic frameworks for hydrogenation of organic cyclic carbonates

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Experimental

Materials

All reagents and solvents were obtained from commercial suppliers and used without further purification.

Synthesis of materials and catalyst

Tetrakis(4-bromo-3-aminophenyl)methane was synthesized using the method described previously.[S1]

Synthesis of PAF-30-NH_2-pre

Tetrakis(4-bromo-3-aminophenyl)methane (500 mg, 0.72 mmol) and biphenyl-4,4′-diyldiboronic acid (349 mg, 1.44 mmol) were placed in a 100 mL round bottomed flask, equipped with stir bar and reflux condenser and then dissolved in DMF (25 mL). After that 4 mL of aqueous K_2CO_3 (2 mol/L) was added followed by quick addition of $Pd(OAc)_2$ (16.2 mg, 0.072 mmol) and PPh_3 (104 mg, 0.397 mmol) after three cycles of evacuation/argon filling. The resulting mixture was refluxed (120°C) for 12 hours. After cooling to room temperature, the precipitate was filtered off and washed with a mixture of 1 mL HNO_3 and 1 mL HCl in 50 mL of water for 10 minutes to remove the palladium residuals. Then it was filtered again and washed with KOH solution (10 wt%, 50 mL×2), water (50 mL×2), THF (150 mL), EtOH (150 mL) and dried under vacuum at 60°C for 8 hours. The product was obtained as a dark-beige powder (350 mg).

Synthesis of Pd-PAF-30-NH_2-pre catalyst

Palladium(II) acetate (4.3 mg, 0.019 mmol) was dissolved in dichloromethane in a 50 mL one-neck flask equipped with a magnetic stir bar and a reflux condenser. Then 100 mg of PAF-30-NH_2-pre was added to the solution, and the mixture was stirred for 24 h. After this, the mixture

was evaporated using a rotary evaporator, and 10 mL of ethanol was added to the dry residue. Then, a cooled solution of $NaBH_4$ (20 mg, 0.53 mmol) in ethanol-water mixture (10 mL, 1:1) was added dropwise, followed by stirring for 24 h. The precipitate was filtered and washed with water (2×50 mL), ethanol (2×50 mL) and dried under vacuum for 6 h.

Catalytic tests

Hydrogenation reactions were performed in a stainless-steel batch reactor equipped with magnetic stirrer. Initially, the autoclave was charged with 5.7 mmol of substrate and 2.5 mg of catalyst. After sealing, the reactor was flushed with H_2 five times, then pressurized to 40 atm with H_2 and heated to 250°C under vigorous mechanical stirring of 800 rpm for 0.5 - 4 h. The autoclave was then cooled to room temperature and depressurized. The reaction products were analysed by gas chromatography with hexadecane as an external standard. All experiments were performed at least twice; the experimental error did not exceed 5%. The substrate conversion, yields and selectivity of products were calculated as follows:

$$Conversion, \% = \frac{mol\ of\ substrate\ charged - mol\ of\ substrate\ left}{mol\ of\ substrate\ charged} \cdot 100\% \quad (1)$$

$$Yield\ (P), \% = \frac{mol\ of\ product(P)}{mol\ of\ substrate\ charged} \cdot 100\% (2)$$

$$Selectivity(P), \% = \frac{mol\ of\ product(P)}{mol\ of\ substrate\ charged - mol\ of\ substrate\ left} \cdot 100\% \quad (3)$$

Characterization

Nitrogen adsorption/desorption isotherms were recorded at 77 K with a Micromeritics Gemini VII 2390 instrument (Micromeritics, Norcross, GA, United States). Sample was degassed at 120 °C for 6 h before measurement. The surface area (S_{BET}) and average pore width (4 V/A) were calculated using the Brunauer–Emmett–Teller (BET) method. The total pore volume (V_{tot}) was determined by the amount of nitrogen adsorbed at a relative pressure of $p/p_o = 0.96$.

Transmission electron microscopy (TEM) analysis was conducted on a JEM-2100 microscope with accelerating voltage of 200 kV. The processing of the micrographs and the calculation of the average particle size were conducted using the ImageJ software program. The analysis was performed in the center “Materials Science and Metallurgy” of NUST MISiS.

The palladium content in the catalyst was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) on a SHIMADZU ICPE-9000 spectrometer in Center for Collective Usage "Analytical Center for the Problems of Deep Refining of Oil and Petrochemistry" of A.V. Topchiev Institute of Petrochemical Synthesis, RAS.

The reaction products were analyzed by gas-liquid chromatography (GC) on an Agilent HP 6890 G1530A chromatograph equipped with a flame ionization detector (FID) and a 30 m× 0.32 mm × 0.5 μm column (DB-WAX). Hydrogen was used as a carrier gas. The chromatograms were recorded and analyzed on a computer using the HP ChemStation Rev. A. 06. 01 (403) package.

Results

Table S1 Porous properties of PAFs

Material	S_{BET}/ m^2g^{-1}	$S_{t\text{-}plot}$/ m^2g^{-1}	$\frac{S_{t-plot}}{S_{BET}}$	V_{pore}/ cm^3g^{-1}	ω_{Het}/ wt.%	Ref.
PAF-30	483	260	0.54	0.37	—	S2
PAF-30-SO_3H	261	—	—	0.26	S – 3.0	S3
PAF-30-NH_2-post	345	—	—	0.20	N – 6.96	S1
PAF-30-NH_2-pre	793	506	0.64	0.55	N – 5.39	This work

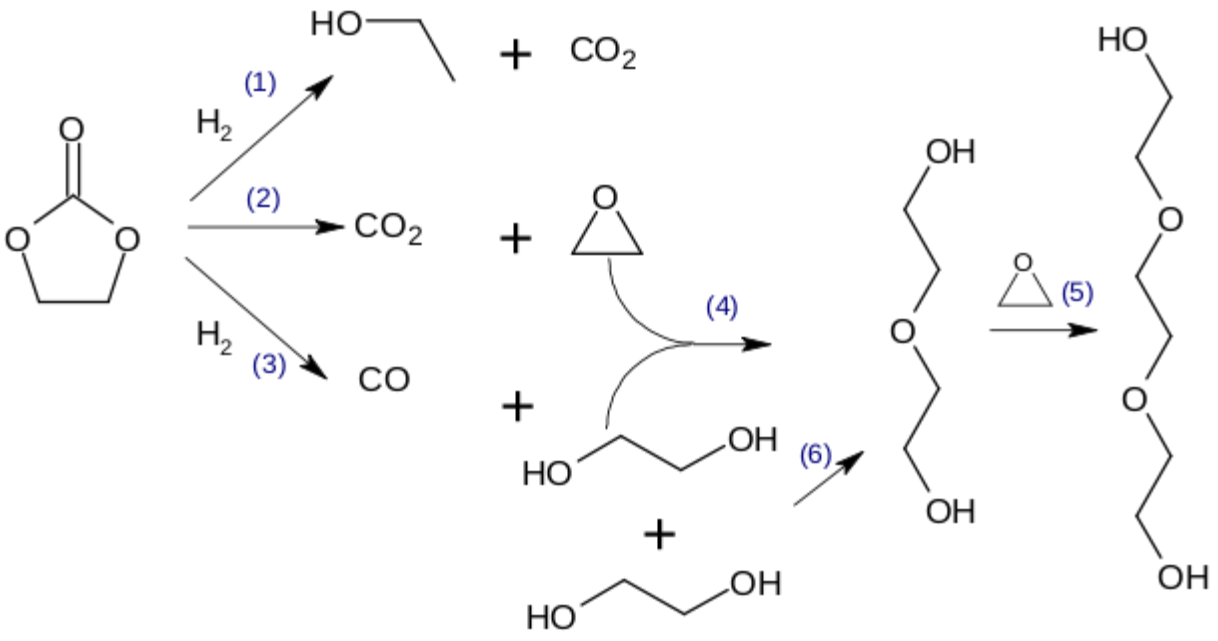

Figure S1 Possible pathways of hydrogenation of EC.

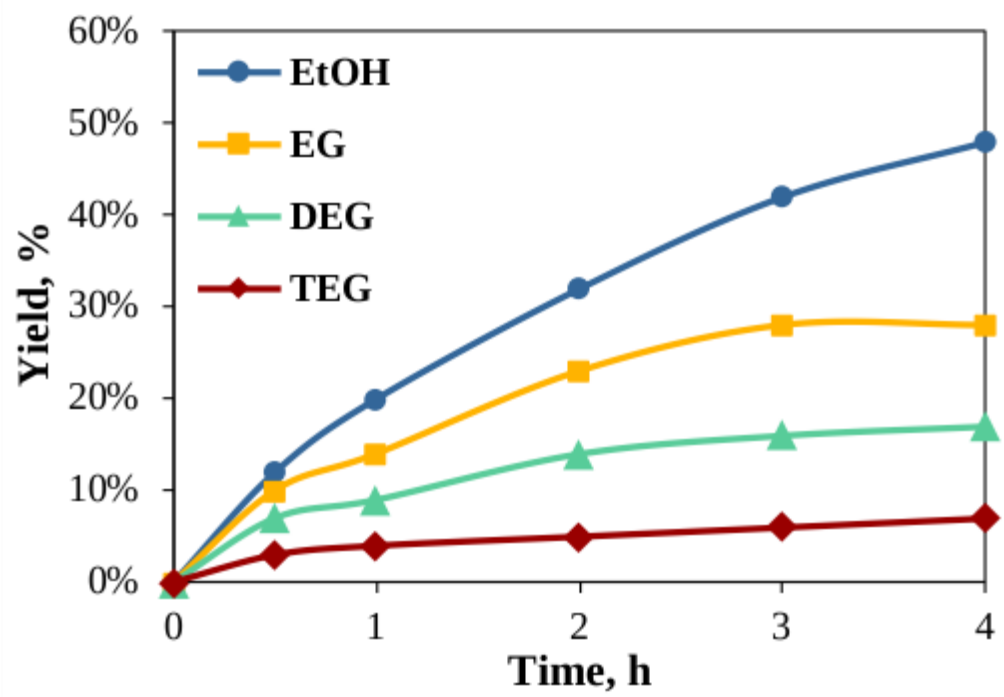

Figure S2 Yields of EC hydrogenation products on Pd-PAF-30-NH_2-pre at different times. *Reaction conditions*: 2.5 mg of the catalyst, 500 mg EC, 40 atm H_2, 250°C.

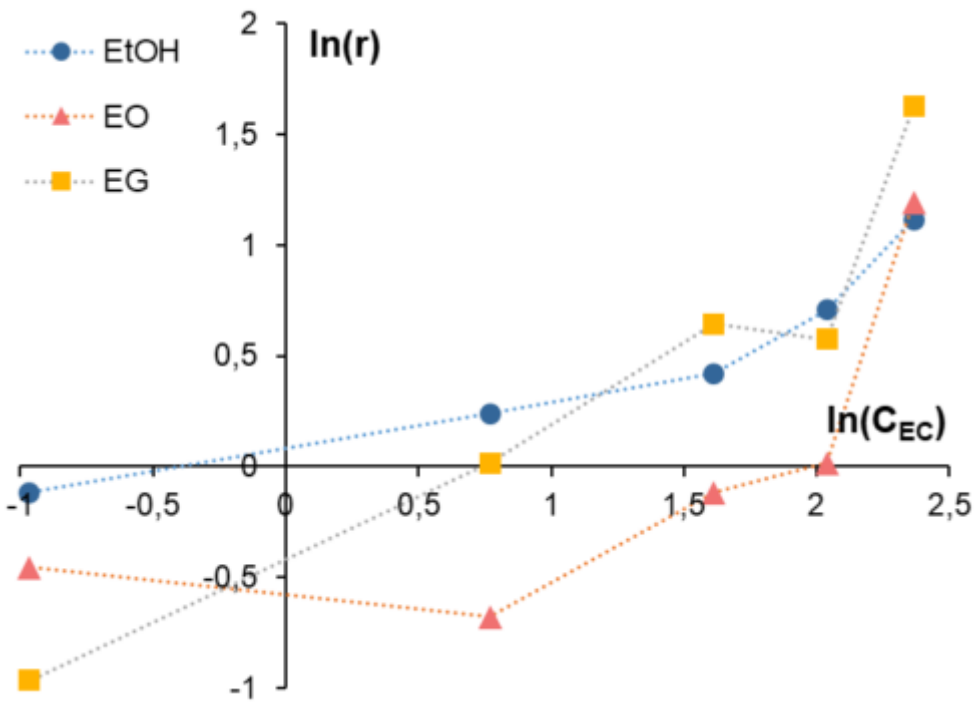

Figure S3 The dependencies ln(r)-ln(C_{EC}) for EtOH, EO and EG.

Since no reaction products were observed when using EG as a substrate, the EC concentration dependences of the rates for reactions №1-3 (Scheme 1) were calculated assuming that DEG and

TEG are formed by reaction with EO: n(EO)=n(DEG)+2·n(TEG); n(EG)*=n(EG)+n(DEG)+ n(TEG).

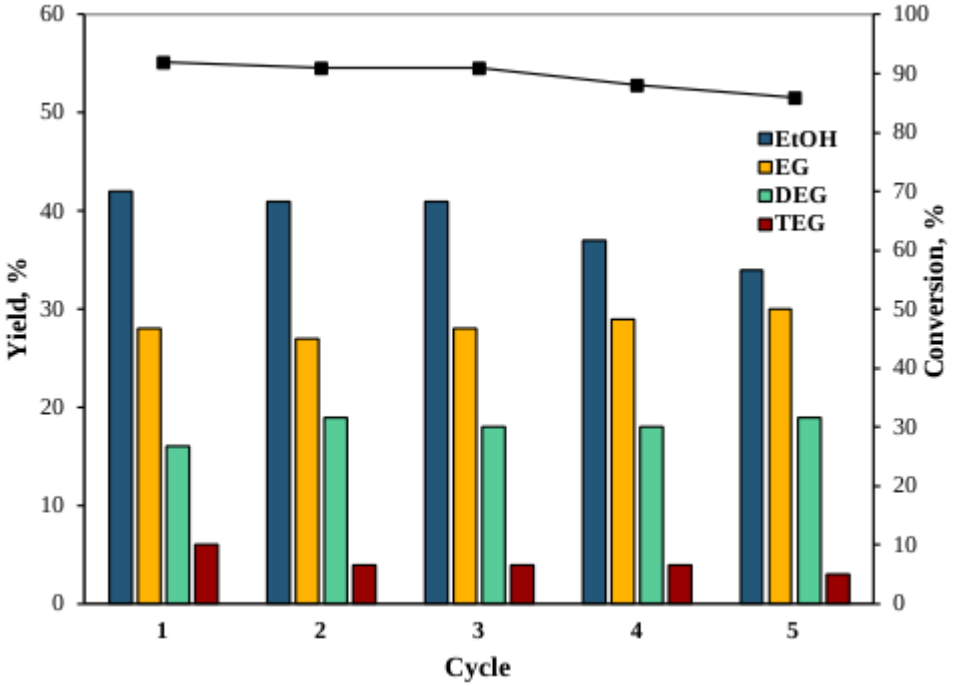

Figure S4 Reusability of Pd-PAF-30-NH_2-pre. *Reaction conditions*: 2.5 mg of catalyst, 500 mg EC, 40 atm H_2, 250℃, 3h.

References

S1. D. Makeeva, L. Kulikov, A. Zolotukhina, A. Maximov and E.Karakhanov, *Mol. Catal*., 2022, **517**, 112012; https://doi.org/10.1016/j.mcat.2021.112012.

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