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Hydrogenation of diverse substrates over covalent triazine framework modified with copper

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The reagents used to prepare CTF-1, *i.e.* 1,4-dicyanobenzene (DCB, purity 99%), zinc chloride (98%) and ethanol rectified (96%), were all purchased from Sigma Aldrich. Solvents and reagents were purified according to standard procedures [V. Zakharov, Y. Kardasheva, V. Chernyshev, M. Terenina, K. Kalmykov, D. Ovsyannikov, S. Savilov, S. Filippova, E. Karakhanov, S. Dunaev, L. Aslanov, *Molec. Catal.*, 2023, **550**, 113598; https://doi.org/10.1016/j.mcat.2023.113598]. Hygroscopic compounds were handled in a SPECS GBVK sealed vacuum glove box (Russia) with a control unit and one gateway; the pressure during pumping was 10^{-2} Torr.

The CTF-1 sample was synthesized by the catalyzed cyclotrimerization using molten $ZnCl_2$. 1,4-Dicyanobenzene (5 g, 39.0 mmol) and $ZnCl_2$ (5 g, 36.7 mmol) were mixed in a mortar in an argon-filled glovebox. Then, the resulting mixture was loaded into a quartz glass ampoule (i.d. 20 mm, length 200 mm). The ampoule was previously dried at 200°C for 1 h. The ampoule was evacuated to a residual pressure of $2.5\cdot10^{-2}$ Torr for 20 min, sealed and then heated in a vertical muffle furnace to 400 °C at a heating rate of 2 K min^{-1} and maintained at 400°C for 40 h. After that, the ampoule was cooled to room temperature and carefully opened under a fume hood using a diamond cutter. The resulting monolith-like black substance was ground in a porcelain cup and then consequentially treated with 0.5 M hydrochloric acid (40 ml), distilled water (2 × 40 ml), and ethanol (2 ×40 ml) for 15 h, respectively. The sample CTF-1 was ultrasonicated in water (4 × 10 min) to enhance zinc chloride removal. The synthesized CTF-1 sample was ultrasonicated using a UZDN-A ultrasonic generator (Russia). Precipitates were separated with a Multi Centrifuge CM 6 M (Elmi Ltd., Latvia) at 3500 rpm. The resulting black powder was dried at 130°C under a vacuum for 5 h. The product yield was 86% based on the initial DCB weight.

Copper was supported on COF by incipient wetness impregnation using copper nitrate, the copper loading was 5 wt. %. The sample was then calcined in argon at 200^{o}C to remove nitrate and then reduced in a hydrogen flow (200^{o}C, 2 h).

Elemental analysis was conducted using a CE1106 CHN analyzer (Carlo Erba, Italy). X-ray powder diffraction patterns of the CTF-1 samples were recorded in the 2θ angle range of 3 – 40^o at room temperature on the EMPYREAN diffractometer equipped with an X'celerator linear detector using Ni-filtered CuK_α radiation. Nitrogen adsorption isotherms were measured using a Micromeritics Gemini VII 2390 surface area analyzer (Micromeritics, USA). All samples were degassed at 120 °C for 8 h before analysis. The crystal size was evaluated by scanning electron microscopy using a BiOptik SEM-69-LV electron microscope with an accelerating voltage of 30 kV. Secondary and backscattered electron detectors were used.

The catalytic experiments were carried out in a Parr autoclave in the temperature range from 100 to 200^{o}C and hydrogen pressure of 10-15 atm. Substrate (20 mmol) was dissolved inethanol (20 ml), the catalyst loading was 100 mg.

The products were analyzed using a CrystaLux 4000M GC instrument equipped with a 30 m × 0.25 mm capillary S2 column Optima-1 (Macherey-Nagel) in the temperature-programmed mode: the column was initially heated to 130 °C, kept at this temperature for 6 min, heated from 130 to 240 °C at a rate 20 °C min^{-1}, and kept at 240 °C for 10 min. According to literature data, substances such as diphenylhydrazine and azobenzene can be formed during hydrogenation of nitrobenzene. These substances are not detected by the GLC method. The side products of phenylacetylene and but-2-yne-1,4-diol hydrogenation are the products of exhaustive hydrogenation.

Table S1 Calculated positions (2□/°) of the main peaks for CTF-1.

hkl parameter	Value
1 0 0	7.32
1 1 0	12.70
2 0 0	14.66
0 0 1	26.19

Table S2 Textural characteristics of the CTF-1 material.

S_{BET} /m^2 g^{-1}	V_{tot}, cm^3 g^{-1}	V_{micro} /cm^3 g^{-1}	V_{meso} /cm^3 g^{-1}	Pore diameter/nm
550	0.30	0.30	0	1.9-2.6

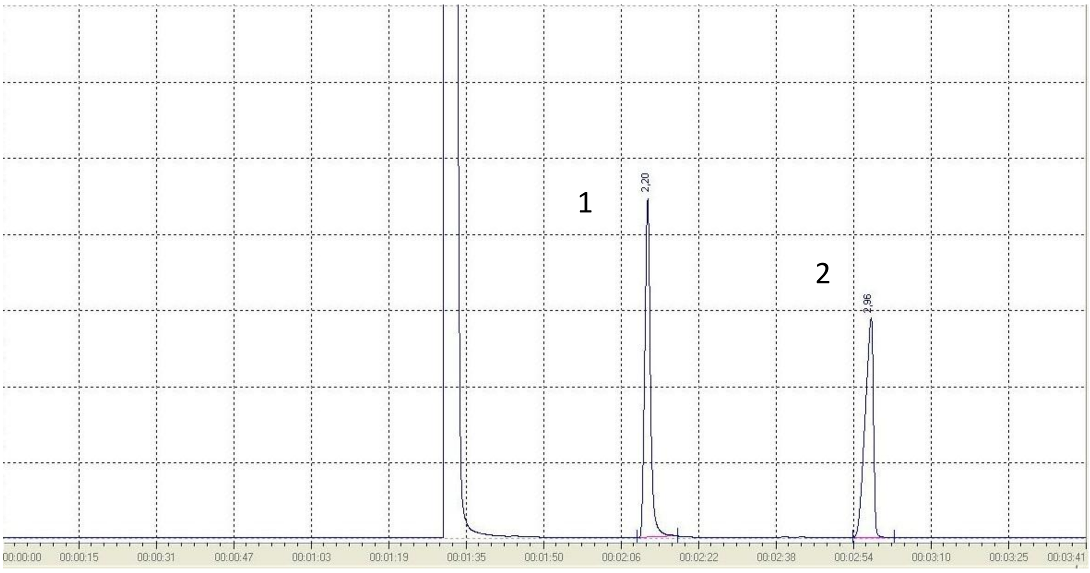

Figure S1 Chromatogram of the initial mixture used for phenylactylene hydrogenation: 1-phenylacetylene, 2-internal standard C_{10}

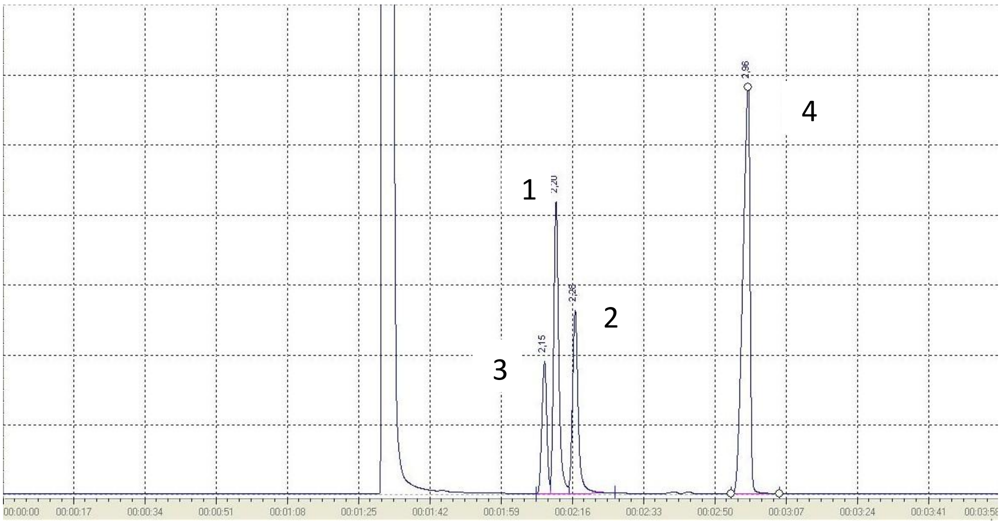

Figure S2 Chromatogram of the products of phenylacetylene hydrogenation: 1-phenylacetylene, 2-styrene, 3-ethylbenzene, 4-internal standard C_{10}

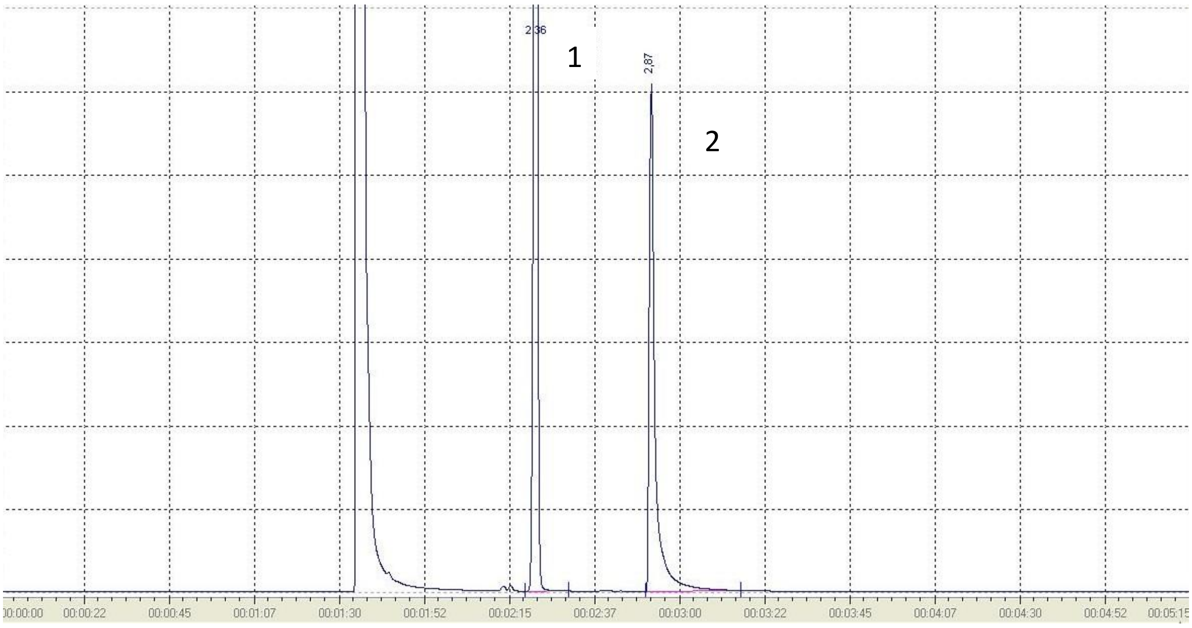

Figure S3 Chromatogram of the initial mixture used for nitrobenzene hydrogenation: 1-nitrobenzene, 2-internal standard C_{10}

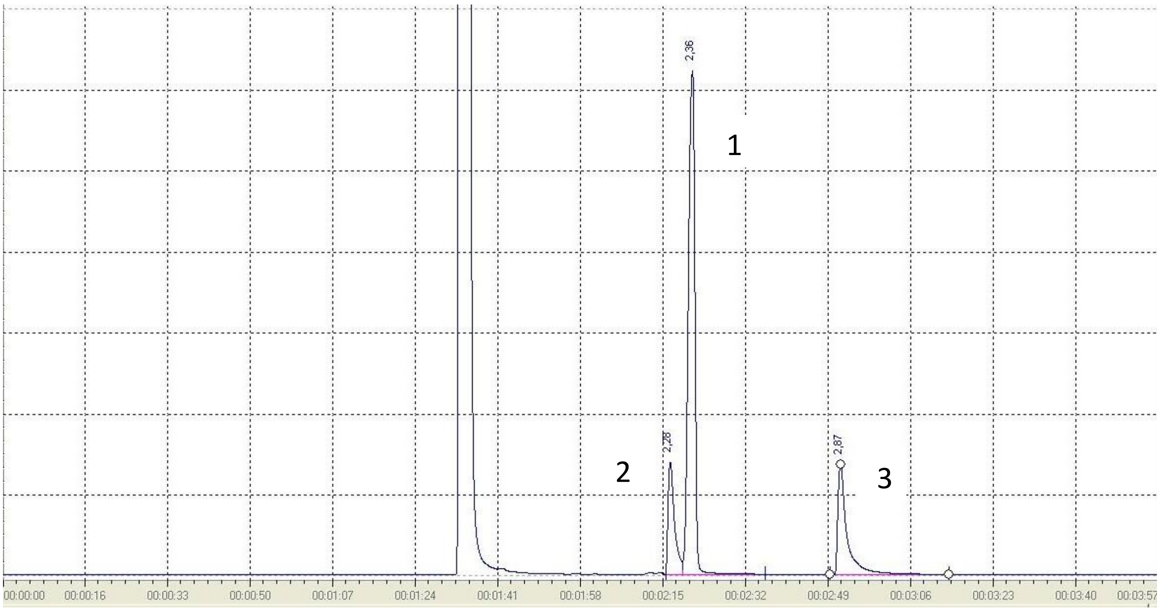

Figure S4 Chromatogram of the products of nitrobenzene hydrogenation: 1-nitrobenzene, 2-aniline, 3-internal standard C_{10}

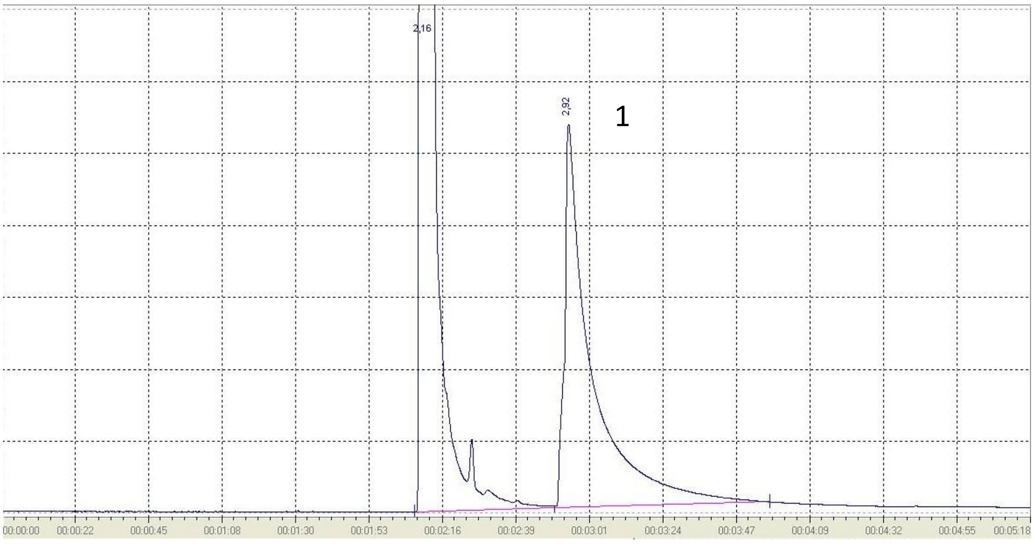

Figure S5 Chromatogram of the initial mixture used for but-2-yne-1,4-diol hydrogenation: 1-but-2-yne-1,4-diol

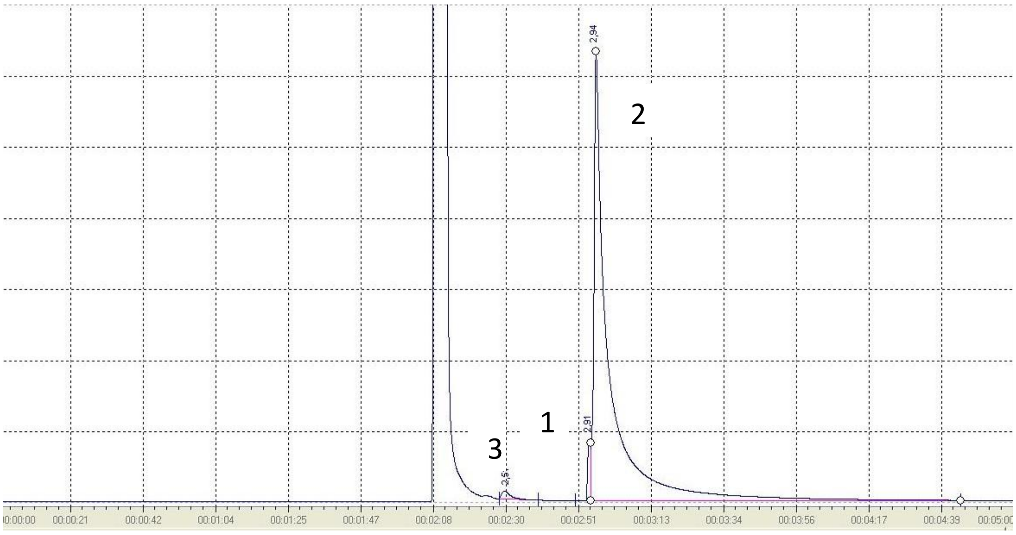

Figure S6 Chromatogram of the products of but-2-yne-1,4-diol hydrogenation: 1-but-2-yne-1,4-diol, 2-*cis*-but-2-ene-1,4-diol, 3-butane-1,4-diol