

Electronic supplementary information

CuPt/MFI CATALYSTS FOR PROPANE DEHYDROGENATION

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Experimental section

Reagents and catalysts

A series of MFI-type zeolites with the nominal SiO₂/Al₂O₃ molar ratios of 80, 280, and 716 (Zeolyst Int.) were used in the H-form after calcination at 600 °C. AR-grade NaCl, Cu(NO₃)₂·3H₂O, and H₂PtCl₆·6H₂O were used for the catalyst preparation. Propane (99.92%) was purchased from BK Group, Russia. The physicochemical properties of the initial zeolites are described in Ref. [1].

Preparation of the catalysts

Example of the MFI-80(3Na)400w150(0.17Cu0.5Pt) catalyst preparation procedure (atomic ratio Cu/Pt=1). An impregnating solution was prepared by dissolving 0.38 g of NaCl in 3 mL of distilled water. The resulting solution and 5 g of a zeolite powder were preheated separately in a water bath to 70 °C. The solution and zeolite were then mixed and held for 1 h under periodical stirring at 70 °C. The mixture was dried at 150 °C for 1 h and calcined in air in a muffle furnace at 400 °C. The powder obtained was mixed with 25 mL of distilled water using a magnetic stirrer at 80 °C for 0.5 h. The product was filtered off without additional washing and dried at 150 °C for 1 h. The sample (4.8 g) was further impregnated with a mixture of 0.03 g of Cu(NO₃)₂·3H₂O, 1.38 g of H₂PtCl₆ solution (18.0 g Pt /L), and 1.55 g of water. After drying at 150 °C for 1 h, the sample was calcined again at 500 °C. The calcination involved heating at a rate of 10 °C/min to 500 °C and keeping at this temperature for 1 h.

Characterization of catalysts

The quantitative elemental analysis was performed by energy dispersive X-ray fluorescence spectroscopy (ED-XRF) using a ThermoScientific ARL Perform'x instrument. The results are presented in Table S1.

The phase composition of the samples was identified by powder X-ray diffraction analysis (XRD) on a TongDaTD-3700 diffractometer with CuK α irradiation.

The Pt dispersion was measured by CO pulse chemisorption using a USGA-101 analyzer. About 200 mg of a sample was placed in a quartz microreactor 4 mm in inner diameter (ID). The sample was heated to 200 °C at a rate of 10 °C/min in a helium flow (10 mL/min) and held at 200 °C for 0.5 h. The gas flow was switched from He to H₂, and the sample was heated in H₂ at 10 °C/min to 540 °C, followed by keeping at this temperature for another 30 min. The reactor was cooled in H₂ to 200 °C, purged with He at 200 °C for 0.5 h, and finally cooled to room temperature in a continuous He flow. For the chemisorption analysis, 0.25 mL pulses of carbon monoxide (CO) diluted to 9.7% in He were injected into a helium flow at 3-min intervals. This was continued until the chemisorption sites reached saturation. The CO concentration at the reactor outlet was monitored by a thermal conductivity detector (TCD). The amount of chemisorbed CO was derived from the TCD signal areas. The Pt dispersion was calculated by the equation:

$$D = \frac{V \cdot AW \cdot SF}{W \cdot 24400} \cdot 100\%,$$

where V is the volume of the adsorbed CO (mL); AW is the atomic weight of Pt (g/mol); SF is the stoichiometric factor (assumed to be equal to 1); and W is the Pt weight in the sample (g).

Table S1. Elemental analyses of the prepared samples (XRFI)

Sample	Si (%)	Al (%)	Na (%)	Cl (%)	Pt (%)	Cu (%)
MFI-80(0.5Pt)	45.69	0.80			0.59	
MFI-80(3Na)400w150(0.5Pt)	44.94	1.06	0.73	0.18	0.51	
MFI-80(3Na)400w150(0.5Cu0.5Pt)	44.65	0.89	0.88	0.29	0.51	0.51
MFI-280(2Na)400w150(0.5Cu0.5Pt)	45.57	0.36	0.32	0.14	0.39	0.57

MFI-716(0.6Na)400w150(0.5Cu0.5Pt)	45.83	0.11	0.20	0.06	0.52	0.57
MFI-80(3Na)150w150(0.8Cu0.3Pt)	44.46	0.94	1.01	0.21	0.27	0.79
MFI-80(3Na)300w300(0.8Cu0.3Pt)	44.05	1.09	1.29	0.35	0.28	0.81
MFI-80(3Na)400w400(0.8Cu0.3Pt)	44.11	1.14	1.17	0.23	0.30	0.87
MFI-80(3Na)500w500(0.8Cu0.3Pt)	43.93	1.04	1.42	0.52	0.33	0.82
MFI-80(3Na)400w150(0.3Pt)	44.83	1.07	1.05	0.17	0.27	
MFI-80(3Na)400w150(0.4Cu0.3Pt)	44.50	1.03	1.12	0.14	0.37	0.40
MFI-80(3Na)400w150(0.8Cu0.3Pt)	44.28	1.06	1.02	0.19	0.32	0.80
MFI-80(3Na)400w150(1Cu0.3Pt)	44.23	1.01	0.96	0.25	0.32	1.05
MFI-80(3Na)400w150(1.6Cu0.3Pt)	43.84	0.99	1.06	0.28	0.32	1.59
MFI-80(3Na)400w150(2.2Cu0.3Pt)	43.40	1.07	1.02	0.30	0.33	2.24
MFI-80(3Na)400w150(0.17Cu0.5Pt)	44.97	0.89	0.71	0.22	0.55	0.17
MFI-80(3Na)400w150(0.3Cu0.1Pt)	44.80	1.13	1.02	0.12	0.09	0.25

The catalytic tests were carried out in a 4-mm ID tubular quartz reactor at 540 °C or 570 °C, 0.1 MPa. 0.05 g of the catalyst was loaded into the reactor, heated in nitrogen to 300 °C at 15 mL/min, then in H₂ at 10 mL/min to the same temperature at which the reaction should be carried out, and held at 540 °C or 570 °C for 0.5 h. The flow was then switched from H₂ to propane with a flow rate of 13 mL/min which corresponds to weight hourly space velocity (WHSV) of 28 h⁻¹.

The PDH reaction was conducted using pure propane without hydrogen or an inert gas. The reaction products were analyzed online on a *Chromatec Crystal 5000* gas chromatograph equipped with a 25-m KCl-Al₂O₃ capillary column and a flame ionization detector (FID).

The propane conversion, reaction product selectivity, and product yields were determined using the following equations:

Propane conversion:

$$X(\%) = \left(1 - \frac{S_{C_3H_8} \cdot k_{C_3H_8}}{\sum_i S_i \cdot k_i} \right) \cdot 100,$$

where $S_{C_3H_8}$ is the peak area of propane (mV·min); S_i is the peak area of product i (mV·min); $k_{C_3H_8}$ is the weight coefficient of propane; and k_i is the weight coefficient of product i .

Product selectivity:

$$S_i(\%) = \frac{S_i \cdot k_i}{\sum_i S_i \cdot k_i} \cdot 100;$$

Product yield:

$$Y_i(\%) = \frac{X \cdot S_i}{100}.$$

The definition of the specific activity (SA) is as follows: the amount of propylene produced, measured in moles, per mole of Pt atoms per second. SA was calculated by the following equation:

$$SA = \frac{\frac{F}{60} \cdot Y_{propylene}}{V_m \cdot \frac{m \cdot \omega_{Pt}}{195}},$$

where F is the propane flow rate (mL/min); V_m is the molar volume of gas (mL/mol); m is the mass of the catalyst (g); ω_{Pt} is the percentage mass content of Pt in the catalyst.

The deactivation constants were calculated using the following equation:

$$K_d = \left(\ln \frac{1 - X_f}{X_f} - \ln \frac{1 - X_{in}}{X_{in}} \right) \cdot t^{-1},$$

where X_{in} is the propane conversion after 1 h on stream; X_f is the propane conversion after t h on stream; and t is the time on stream (h).

The catalyst index of productivity (IP) was used as a benchmark for comparison [2], which is calculated as follows:

$$IP = \frac{SA}{K_d}$$

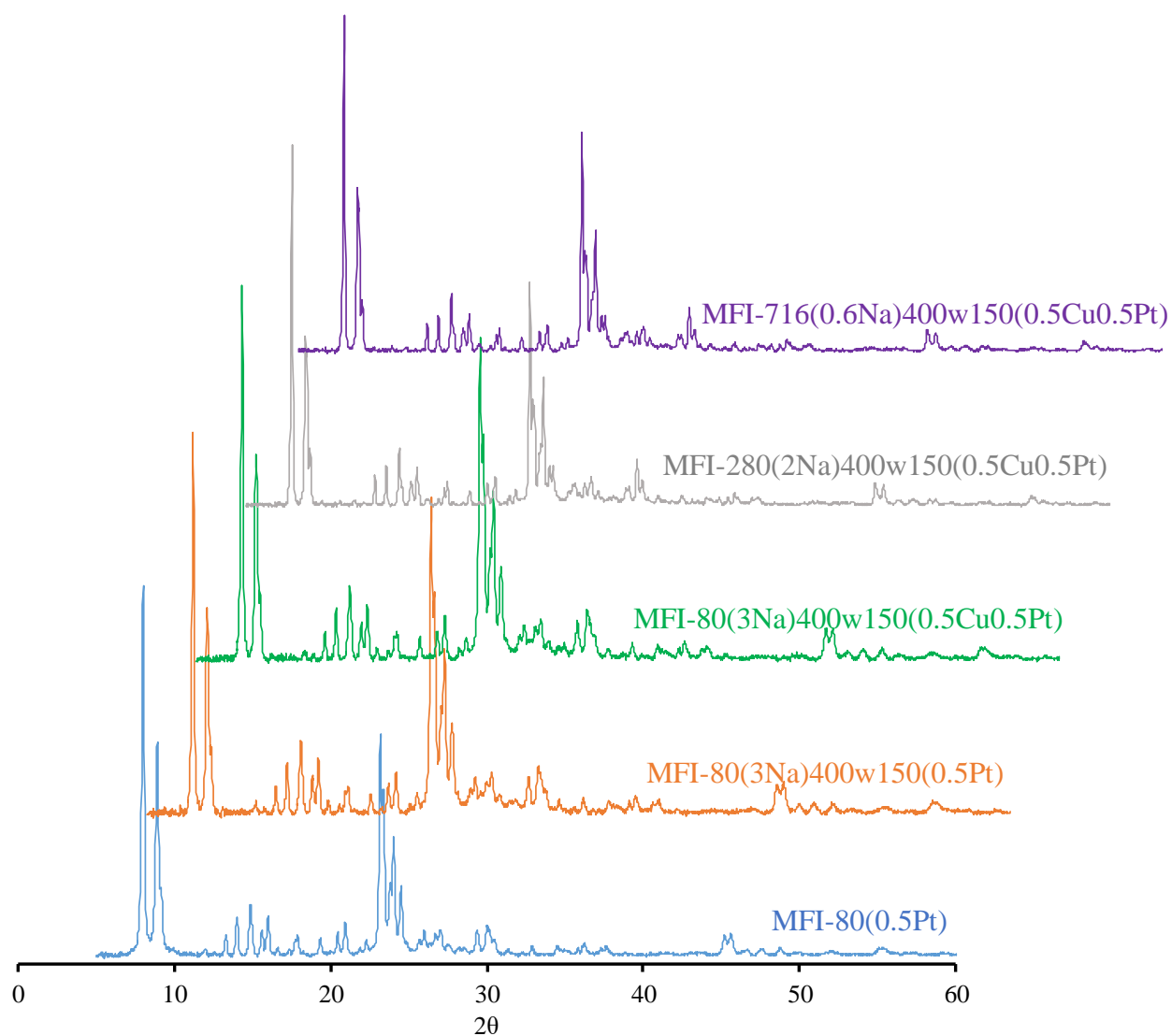


Figure S1. XRD patterns of some ICW catalysts.

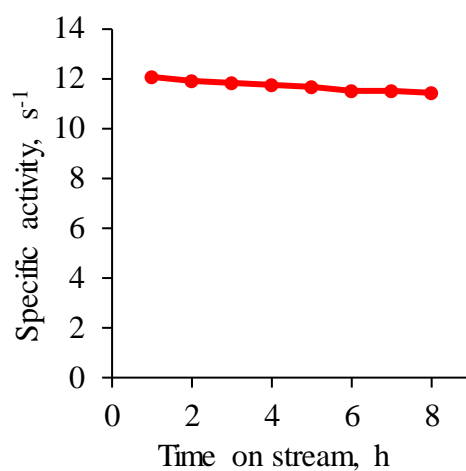


Figure S2. Specific activity for MFI-80(3Na)400w150(0.3Cu0.1Pt) catalyst.
The PDH reaction conditions: 570 °C, 0.1 MPa, 28 h⁻¹.

References

1. A. B. Ponomaryov, A. V. Smirnov, E. V. Pisarenko, M. V. Shostakovsky, *Microporous Mesoporous Mater.*, **2022**, 339, 112010. DOI: 10.1016/j.micromeso.2022.112010
2. A. B. Ponomaryov, A. V. Smirnov, E. V. Pisarenko, M. V. Shostakovsky, *Appl. Catal., A*, **2024**, 673, 119588. DOI: 10.1016/j.apcata.2024.119588