**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 Cu*K*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:

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 (XRFl)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| 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 veloсity (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:

where is the peak area of propane (mV·min); is the peak area of product *i* (mV·min); is the weight coefficient of propane; and is the weight coefficient of product *i*.

Product selectivity:

Product yield:

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:

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

The deactivation constants were calculated using the following equation:

where is the propane conversion after 1 h on stream; 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:



MFI-80(0.5Pt)

MFI-80(3Na)400w150(0.5Pt)

MFI-80(3Na)400w150(0.5Cu0.5Pt)

MFI-280(2Na)400w150(0.5Cu0.5Pt)

MFI-716(0.6Na)400w150(0.5Cu0.5Pt)

**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