**Electronic supplementary information**

**Influence of divalent metal promoters on  
the Pt dispersion and performance of the Pt/MFI  
propane dehydrogenation catalysts**

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**Experimental section**

**Reagents and catalysts**

MFI-type zeolite with the nominal SiO2/Al2O3 molar ratio of 80 (Zeolyst Int.) was used in the H-form after calcination at 600 °C. AR-grade NaCl, CaCl2·6H2O, MgCl2·6H2O, ZnCl2, MnCl2·4H2O, CoCl2·6H2O, CuCl2·2H2O, NiCl2·6H2O, SnCl2·2H2O, 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**

All catalysts were prepared with the promoter/Pt atomic ratio of about 3 (Table S1).

**Example of the (3Na)400w150(0.4Mn0.5Pt) catalyst preparation procedure (atomic ratio Mn/Pt = 2.8).** 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 (1.0 g) was further impregnated with a mixture of 0.015 g of MnCl2·4H2O, 0.32 g of H2PtCl6 solution (13.2 g Pt/L), and 0.28 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 the catalysts**

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

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

The Pt dispersion was measured by CO pulse chemisorption using a USGA-101 analyzer. About 200 mg of the 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).

**The catalytic tests** were carried out in a 4-mm ID tubular quartz reactor at 540 °C, 0.1 MPa. The catalyst sample (0.05 g) was loaded into the reactor, heated in nitrogen to 300 °C at 15 mL/min, then in H2 to 540 °C at 10 mL/min, and held at 540 °C for 0.5 h. The flow was then switched from H2 to propane with a flow rate of 13 mL/min (WHSV=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 as follows.

Propane conversion:

X = %;

Product selectivity:

Si = ;

Product yield:

Yi = Si·X

The specific activity was defined as moles of propylene produced by 1 mol of Pt atoms per second.

The deactivation constants were calculated using the following equation:

,

where *t* is the time on stream, *X*in is the propane conversion after 1 h on stream, *X*f is the propane conversion at the end of the experiment.

A higher deactivation constant indicates a faster loss of the catalyst activity.

The catalyst index of productivity (*IP*) was used as a benchmark for comparison [2], which was calculated using the following equation:

,

where *SA* is the specific activity expressed in s–1, *K*d is the deactivation constant expressed in h–1.

**Table S1.** Chemical compositions of the catalyst samples derived from MFI-80 zeolite

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample | | Element content, wt % (XRFl) | | | | M:Pt atomic ratio |
| Promoter М | Name | Na | M | Pt | Cl |
| no | (3Na)400w150(0.5Pt) | 0.73 | – | 0.51 | 0.18 | – |
| Ca | (3Na)400w150(0.3Ca0.5Pt) | 0.68 | 0.29 | 0.55 | 0.42 | 2.60 |
| Mg | (3Na)400w150(0.2Mg0.5Pt) | 0.74 | 0.17 | 0.57 | 0.29 | 2.43 |
| Mn | (3Na)400w150(0.4Mn0.5Pt) | 0.65 | 0.42 | 0.53 | 0.26 | 2.82 |
| Zn | (3Na)400w150(0.5Zn0.5Pt) | 0.87 | 0.52 | 0.43 | 0.35 | 3.37 |
| Co | (3Na)400w150(0.5Co0.5Pt) | 0.94 | 0.52 | 0.51 | 0.28 | 3.37 |
| Cu | (3Na)400w150(0.50Cu0.5Pt) | 0.88 | 0.51 | 0.51 | 0.29 | 3.06 |
| Ni | (3Na)400w150(0.5Ni0.5Pt) | 0.81 | 0.43 | 0.52 | 0.32 | 2.70 |
| Sn | (3Na)400w150(0.9Sn0.5Pt) | 0.81 | 0.87 | 0.47 | 0.24 | 3.06 |



**Figure S1**. XRD patterns of 0.5Pt-based samples derived from MFI-80 zeolite  
with and without Na, Mg, Cu.



**Figure S2.** Effect of divalent promoters on the propylene yield and selectivity to propylene in PDH reaction. The reaction conditions: WHSV = 28 h–1, 540 °C, 0.1 MPa.

**Table S2.** Catalytic performance of some MPt catalysts for propane dehydrogenation reported to date in comparison with the catalysts prepared in the present study

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Catalyst | WHSV, h–1 | *Т*, °С | C3H6 yield, % | Feed composition | Pt, % | Time on stream, h | Specific activity, s–1 ***a*** | Deactivation constant, h– | IP***b*** | Ref. |
| Pt0Znδ+/SiO2 | 75 | 550 | 30 | C3H8/Ar = 1/4 | 3.05 | 30 | 0.96 | 0.027 | 35 | [3] |
| K-PtSn@MFI-H2 | 27 | 600 | 68 | C3H8/ N2 = 1/3.3 | 0.40 | 25 | 3.31 | 0.022 | 150 | [4] |
| 0.1Pt0.4CuK@S-1 | 5.4 | 550 | 40 | C3H8/N2 = 1/3 | 0.16 | 73 | 1.73 | 0.005 | 355 | [5] |
| (3Na0.5Sn)w(0.25Pt) | 28 | 570 | 35 | pure C3H8 | 0.24 | 8 | 5.30 | 0.013 | 404 | [6] |
| (3Na)400w150(0.5Zn0.5Pt) | 28 | 540 | 27 | pure C3H8 | 0.43 | 8 | 2.26 | 0.004 | 514 | This work |
| (3Na)400w150(0.50Cu0.5Pt) | 30 | 0.51 | 2.10 | 0.020 | 106 |
| (3Na)400w150(0.9Sn0.5Pt) | 22 | 0.47 | 1.68 | 0.024 | 71 |
| (3Na)400w150(0.4Mn0.5Pt) | 28 | 0.53 | 1.94 | 0.031 | 64 |
| (3Na)400w150(0.5Co0.5Pt) | 29 | 0.51 | 2.04 | 0.043 | 47 |
| (3Na)400w150(0.2Mg0.5Pt) | 28 | 0.57 | 1.77 | 0.038 | 47 |
| (3Na)400w150(0.5Ni0.5Pt) | 27 | 0.52 | 2.08 | 0.048 | 44 |
| (3Na)400w150(0.3Ca0.5Pt) | 28 | 0.55 | 1.84 | 0.047 | 39 |
| (3Na)400w150(0.5Pt) | 24 | 0.51 | 1.72 | 0.062 | 28 |

***a*** specific activity is defined as the moles of C3H6 formation per Pt g-atom per second;

***b*** IP (index of productivity) is thespecific activity/deactivation constant [7].

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