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 SiO_2/Al_2O_3 molar ratio of 80 (Zeolyst Int.) was used in the H-form after calcination at 600 °C. AR-grade NaCl, $CaCl_2 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$, $ZnCl_2$, $MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, $SnCl_2 \cdot 2H_2O$, and $H_2PtCl_6 \cdot 6H_2O$ 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 $MnCl_2 \cdot 4H_2O$, 0.32 g of H_2PtCl_6 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$K\alpha$ 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 H_2, and the sample was heated in H_2 at 10 °C/min to 540 °C, followed by keeping at this temperature for another 30 min. The reactor was cooled in H_2 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).

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 H_2 to 540 °C at 10 mL/min, and held at 540 °C for 0.5 h. The flow was then switched from H_2 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-Al_2O_3 capillary column and a flame ionization detector (FID).

The propane conversion, reaction product selectivity, and product yields were determined as follows.
Propane conversion:

$$X = \frac{mass\ \ of\ propane\ in\ the\ feed - mass\ of\ propane\ in\ the\ product}{mass\ \ of\ propane\ in\ the\ feed} \cdot 100\%;$$

Product selectivity:

$$S_i = \frac{mass\ of\ product\ i}{mass\ \ of\ all\ products} \cdot 100\%;$$

Product yield:

$$Y_i = S_i \cdot X/100$$

The specific activity was defined as moles of propylene produced by 1 mol of Pt atoms per second.
The deactivation constants K_d were calculated using the following equation:

$$K_d * t = \ln(\frac{(1-X_f)/X_f}{(1-X_{in})/X_{in}}),$$

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:

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

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 M	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

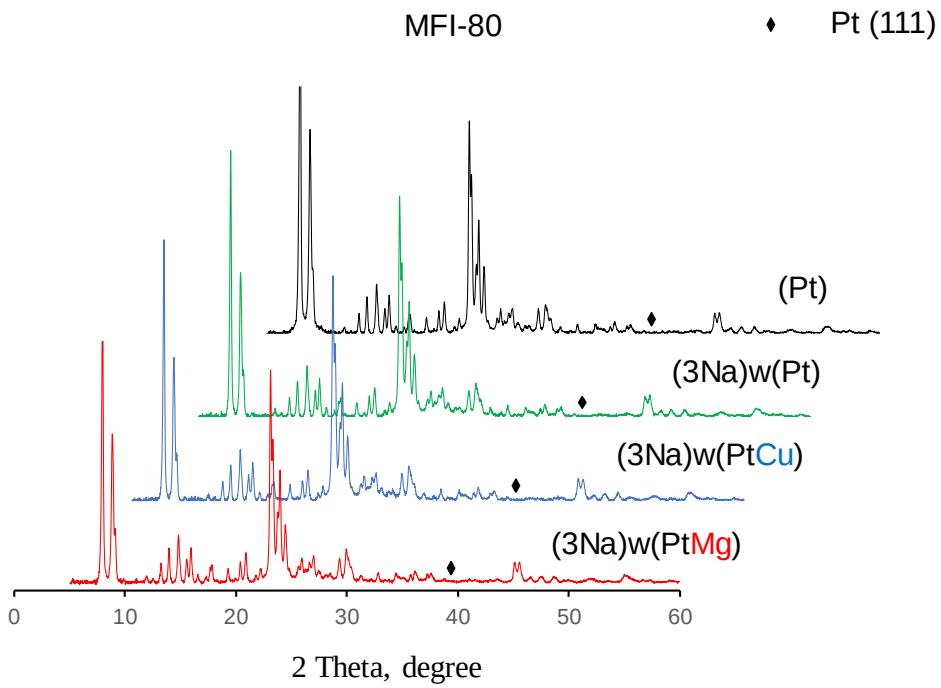

Figure S1. XRD patterns of 0.5Pt-based samples derived from MFI-80 zeolite with and without Na, Mg, Cu.

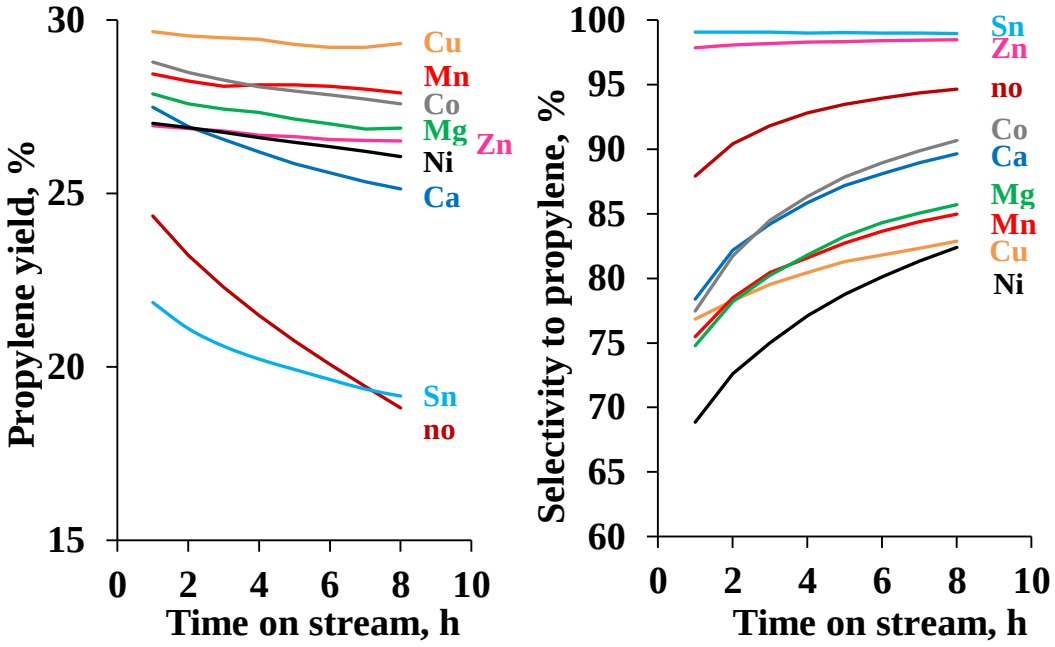

Figure S2. Effect of divalent promoters on the propylene yield and selectivity to propylene in PDH reaction. The reaction conditions: WHSV = 28 h^{-1}, 540 °C, 0.1 MPa.

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}	*T*, °C	C_3H_6 yield, %	Feed composition	Pt, %	Time on stream, h	Specific activity, s^{-1} [a]	Deactivation constant, h^{-}	IP[b]	Ref.
$Pt^0Zn^{\delta+}/SiO_2$	75	550	30	C_3H_8/Ar = 1/4	3.05	30	0.96	0.027	35	[3]
K-PtSn@MFI-H2	27	600	68	C_3H_8/ N_2 = 1/3.3	0.40	25	3.31	0.022	150	[4]
0.1Pt0.4CuK@S-1	5.4	550	40	C_3H_8/N_2 = 1/3	0.16	73	1.73	0.005	355	[5]
(3Na0.5Sn)w(0.25Pt)	28	570	35	pure C_3H_8	0.24	8	5.30	0.013	404	[6]
(3Na)400w150(0.5Zn0.5Pt)			27		0.43		2.26	0.004	514	
(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)	28	540	29	pure C_3H_8	0.51	8	2.04	0.043	47	This work
(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 C_3H_6 formation per Pt g-atom per second;

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

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