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Supplementary materials

Selective Hydrogenation of 2-Methyl-3-butyn-2-ol in Microcapillary Reactor on Supported Intermetallic PdZn Catalyst, Effect of Support Doping on Stability and Kinetic Parameters

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Table S1. Kinetic parameters of the hydrogenation reaction of MBY on films PdZn/TiO_2 after different pretreatments.

Parameter	PdZn/TiO_2-a	PdZn/TiO_2-b	PdZn/TiO_2-c	PdZn/TiO_2-d
k_1/mol/L/s/g_{Pd}'	714	579	1200	920
k_2'/mol/L/s/g_{Pd}	132	177	310	1752
k_3'/mol/L/s/g_{Pd}	20	1.0	20	5×10^{-6}
K_{MBY}, L/mol	61	49	45	90
K_{MBE}	0.8	0.8	0.8	0.8
K_{MBA}	8	1.8	0.1	0.001
K_{MBE}/K_{MBY}	0.013	0.016	0.018	0.009
K_{MBA}/K_{MBE}	10	2.3	0.125	1.3×10^{-3}
K_{MBA}/K_{MBY} [1]	0.13	0.04	2.2×10^{-3}	1.1×10^{-5}
Max/deviation,%	20	25	16	11
Q, g_{MBE}/day	3.6	3.6	3.4	2.8
S_{97},%	96.7	97.1	97.3	94.8

Table S2. Kinetic parameters of the hydrogenation reaction of MBY on films PdZn/$Ti_{0.8}Zr_{0.8}O_2$ after different pretreatments.

Parameter	PdZn/$Ti_{0.8}Zr_{0.8}O_2$-a	PdZn/$Ti_{0.8}Zr_{0.8}O_2$-b	PdZn/$Ti_{0.8}Zr_{0.8}O_2$-c	PdZn/$Ti_{0.8}Zr_{0.8}O_2$-d
k_1'/mol/L/s/g_{Pd}	788	1416	1469	798
k_2'/mol/L/s/g_{Pd}	176	978	1199	1291
k_3'/mol/L/s/g_{Pd}	41	8	30	9
K_{MBY}, L/mol	43	16	20	48
K_{MBE} [1]	0.6	0.6	0.6	0.6
K_{MBA}	0.01	0.0001	0.0001	0.0001

[1] Fixed value.

K_{MBE}/K_{MBY}	0.014	0.038	0.030	0.013
K_{MBA}/K_{MBE}	0.017	1.7×10^{-4}	1.7×10^{-4}	1.7×10^{-4}
K_{MBA}/K_{MBY^2}	2.3×10^{-4}	6.3×10^{-6}	5.0×10^{-6}	2.1×10^{-6}
Max/deviation,%	24	19	22	20
Q, gMBE/day	6.3	12.5	4.8	4.6
S_{97},%	96.8	93.4	92.3	94.0

Table S3. Kinetic parameters of the hydrogenation reaction of MBY on films PdZn/$Ti_{0.95}Ce_{0.05}O_2$ after different pretreatments.

Parameter	**PdZn/$Ti_{0.95}Ce_{0.05}O_2$-a**	**PdZn/$Ti_{0.95}Ce_{0.05}O_2$-b**	**PdZn/$Ti_{0.95}Ce_{0.05}O_2$-c**	**PdZn/$Ti_{0.95}Ce_{0.05}O_2$-d**
k_1'/mol/L/s/g_{Pd}	1357	1943	1537	1695
k_2'/mol/L/s/g_{Pd}	1012	568	296	863
k_3'/mol/L/s/g_{Pd}	0.0001	20	35	0.8
$K_{MBY'}$ L/mol	32	58	50	62
K_{MBE}	1	1	1	1
K_{MBA}	0.001	0.01	0.1	0.0001
K_{MBE}/K_{MBY}	0.031	0.017	0.02	0.016
K_{MBA}/K_{MBE}	0.001	0.01	0.1	0.0001
K_{MBA}/K_{MBY^2}	3.1×10^{-5}	1.7×10^{-4}	1.6×10^{-3}	1.6×10^{-6}
Max/deviation,%	16	25	17	21
Q, gMBE/day	3.7	2.1	3.4	1.2
S_{97},%	93.7	97.3	96.8	97.1

Table S4. Kinetic parameters of the hydrogenation reaction of MBY on films PdZn/$Ti_{0.8}Zn_{0.2}O_{1.7}$ after different pretreatments.

Parameter	**PdZn/$Ti_{0.8}Zn_{0.2}O_{1.7}$-a**	**PdZn/$Ti_{0.8}Zn_{0.2}O_{1.7}$-b**	**PdZn/$Ti_{0.8}Zn_{0.2}O_{1.7}$-c**	**PdZn/$Ti_{0.8}Zn_{0.2}O_{1.7}$-d**
k_1'/mol/L/s/g_{Pd}	244	919	791	788
k_2'/mol/L/s/g_{Pd}	24	53	67	151
k_3'/mol/L/s/g_{Pd}	7	22	6	7
$K_{MBY'}$ L/mol	52	49	42	48
K_{MBE}	0.3	0.3	0.3	0.3
K_{MBA}	1	0.00016	0.001	0.0001
K_{MBE}/K_{MBY}	0.006	0.006	0.007	0.006
K_{MBA}/K_{MBE}	3.3	5×10^{-4}	3×10^{-3}	3×10^{-4}
K_{MBA}/K_{MBY^2}	0.02	3×10^{-6}	2×10^{-5}	2×10^{-6}
Max/deviation,%	28	17	15	13
Q, gMBE/day	0.42	1.3	2.5	1.0
S_{97},%	97.4	97.6	99.0	98.8

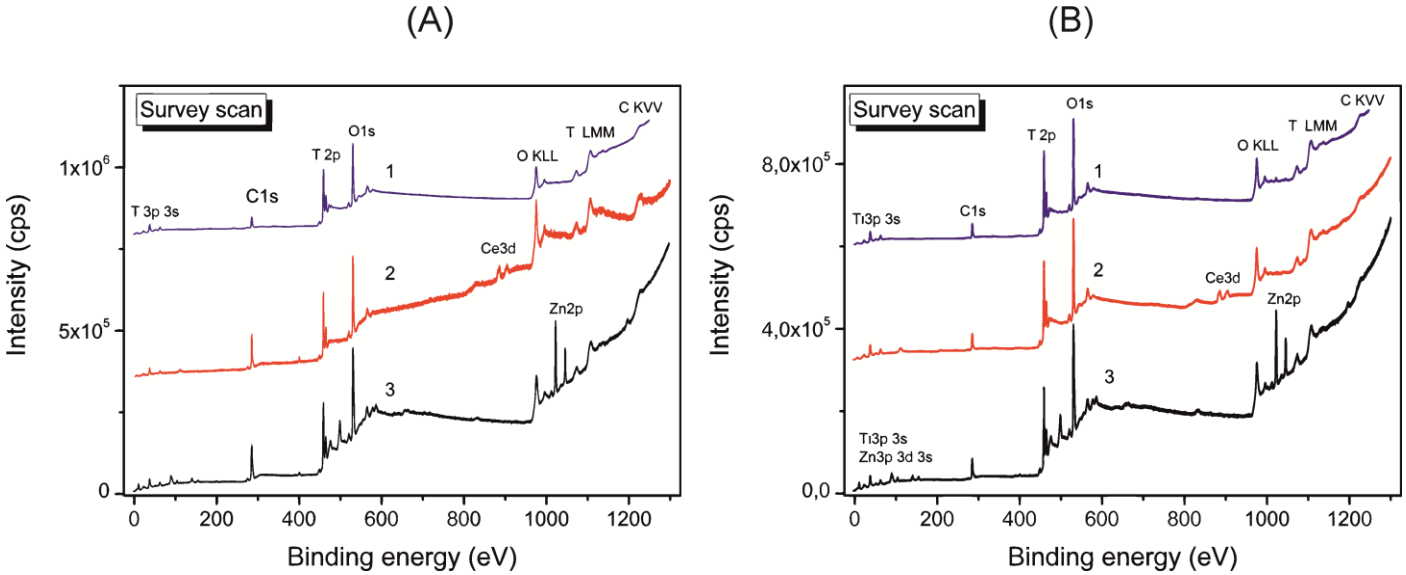

Figure S1. Survey spectra of the catalysts after (A) reduction with 30 vol.% hydrogen in argon at 573 K for 2 h and (B) calcination at 573 K in air and reduction with 30 vol.% hydrogen in argon at 573 K for 2 h. PdZn/TiO_2 (1), PdZn/$Ti_{0.95}Ce_{0.05}O_2$ (2), PdZn/$Ti_{0.8}Zn_{0.2}O_{1.8}$ (3).

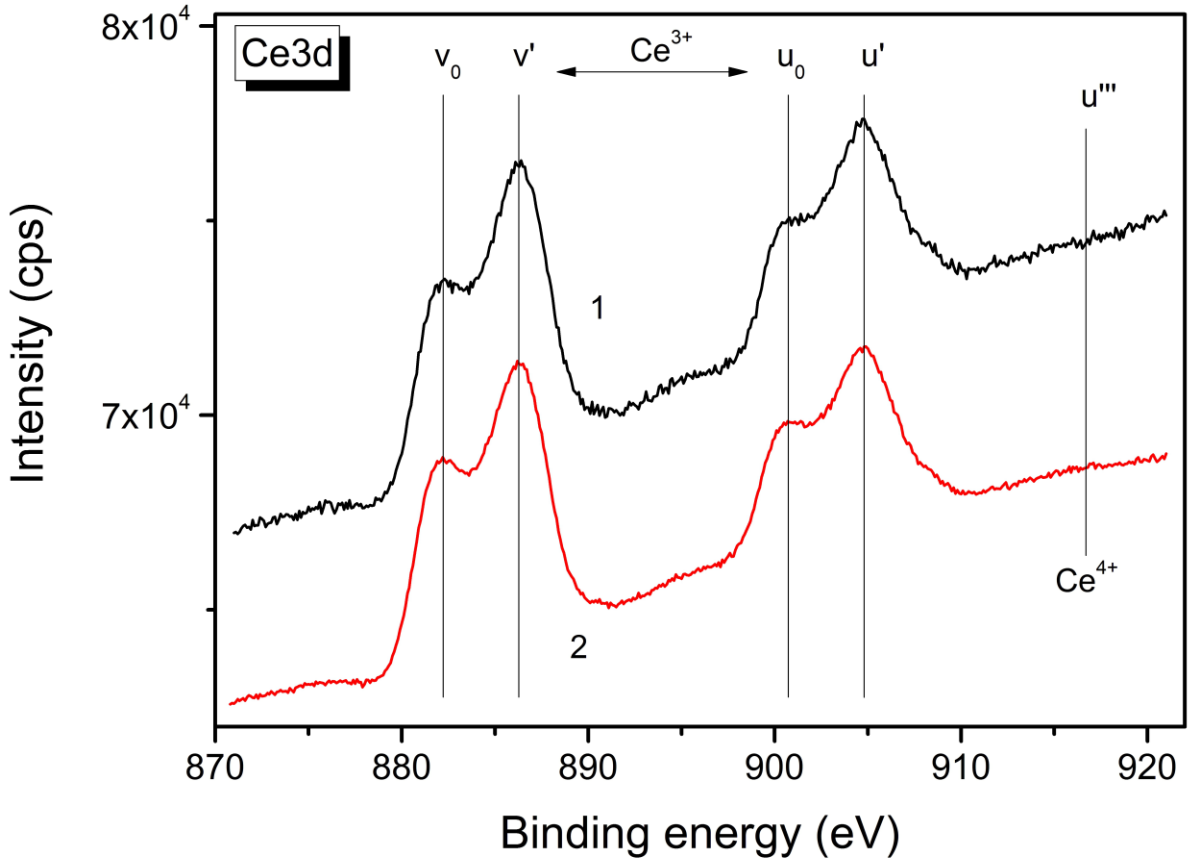

Figure S2. Ce3d core-level X-ray photoelectron spectra of PdZn/$Ti_{0.95}Ce_{0.05}O_2$ after reduction with 30 vol.% hydrogen in argon at 573 K for 2 h (1) and calcination at 573 K in air and reduction with 30 vol.% hydrogen in argon at 573 K for 2 h (2).

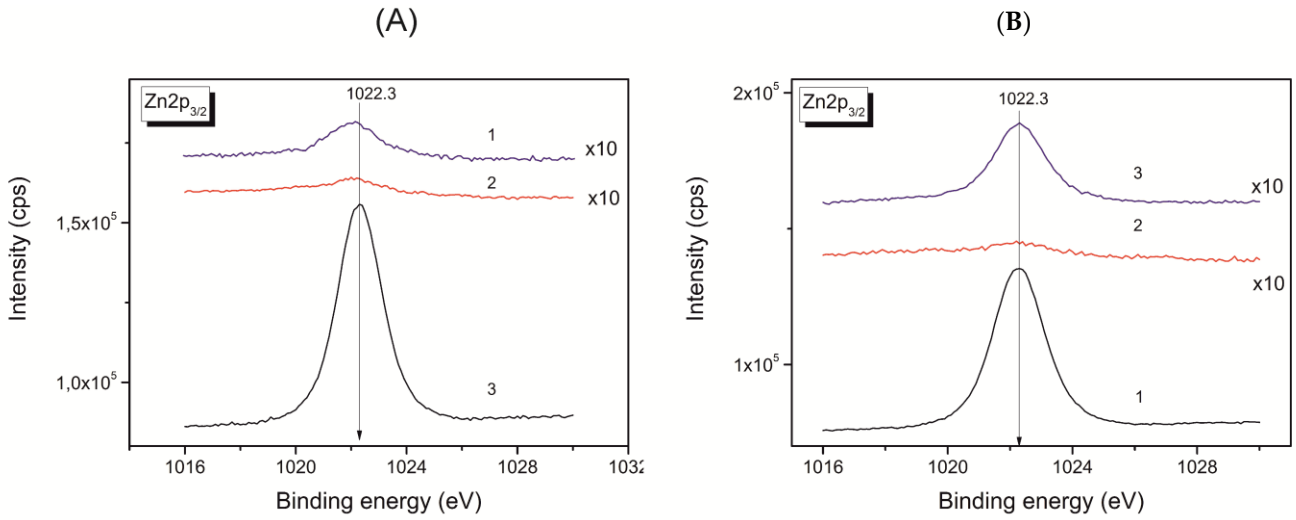

Figure S3. Zn $2p_{3/2}$ core-level X-ray photoelectron spectra of PdZn/$Ti_{0.95}Ce_{0.05}O_2$ after (A) reduction with 30 vol.% hydrogen in argon at 573 K for 2 h and (B) calcination at 573 K in air and reduction with 30 vol.% hydrogen in argon at 573 K for 2 h. PdZn/TiO_2 (1), PdZn/$Ti_{0.95}Ce_{0.05}O_2$ (2), PdZn/$Ti_{0.8}Zn_{0.2}O_{1.8}$ (3).

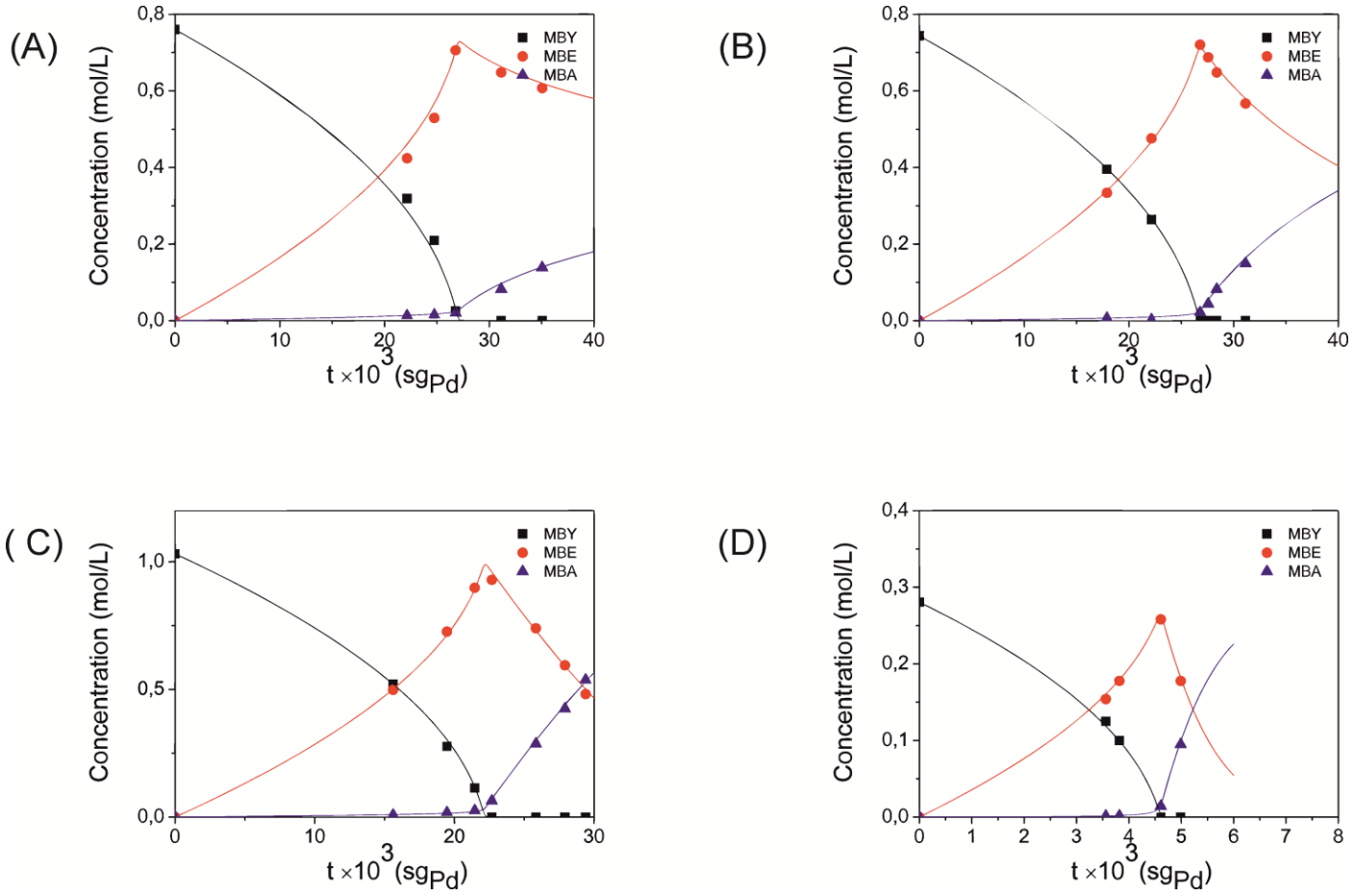

Figure S4. Dependences of the concentrations of MBY, MBE and MBA on the contact time after different pretreatments on PdZn/TiO_2 -a (A), PdZn/TiO_2-b (B), PdZn/TiO_2-c (C), PdZn/TiO_2-d (D), points - experiment, lines - calculation by the Langmuir-Hinshelwood model. Reaction conditions: gas flow rate 6.0 mL / min, = 1 atm, T = 313 K.

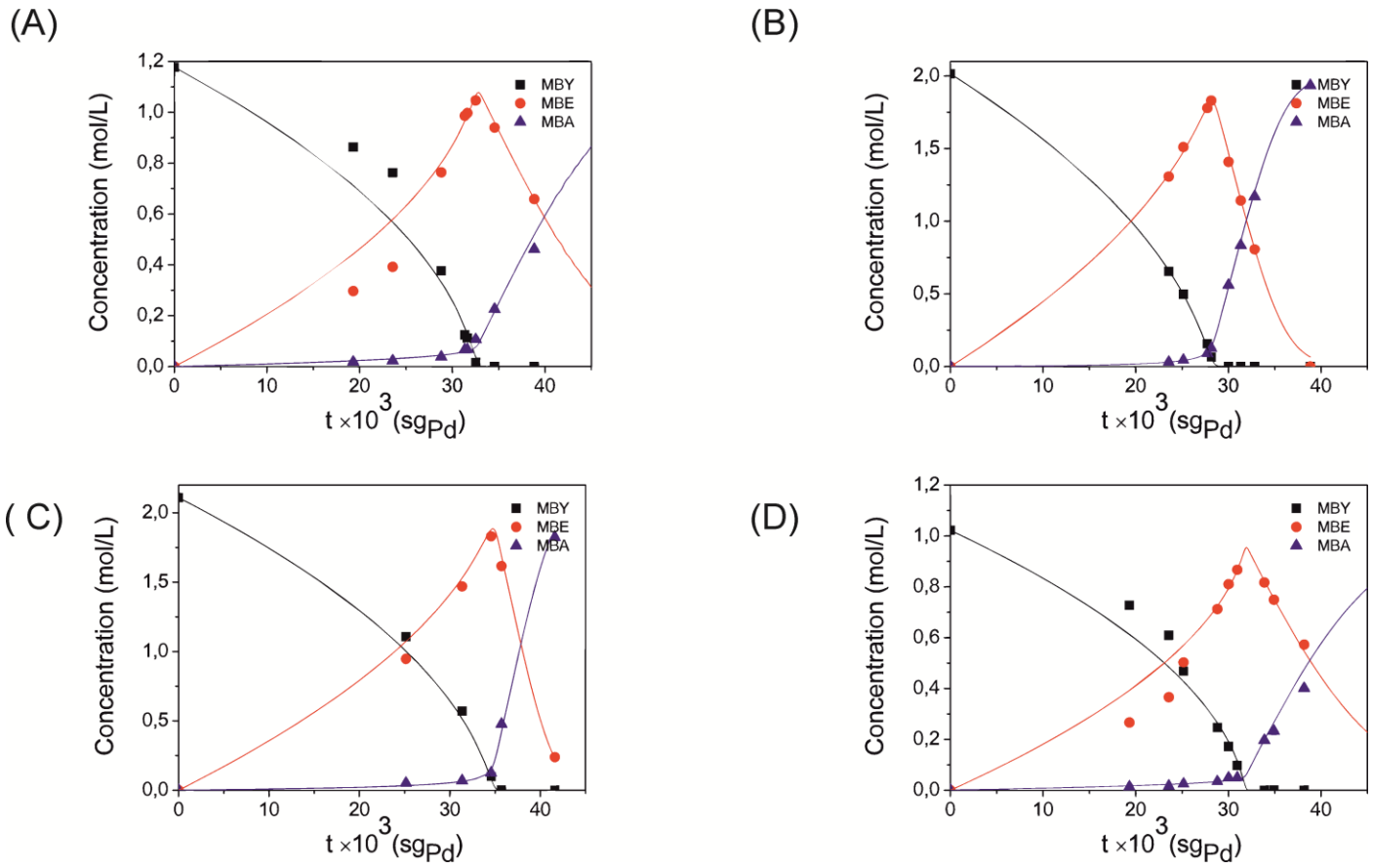

Figure S5. Dependences of the concentrations of MBY, MBE and MBA on the contact time after different pretreatments on PdZn/$Ti_{0.8}Zr_{0.8}O_2$ -a (A), PdZn/$Ti_{0.8}Zr_{0.8}O_2$ -b (B), PdZn/$Ti_{0.8}Zr_{0.8}O_2$ -c (C), PdZn/$Ti_{0.8}Zr_{0.8}O_2$ -d (D), points - experiment, lines - calculation by the Langmuir-Hinshelwood model. Reaction conditions: gas flow rate 6.0 mL/min, = 1 atm, T = 313 K.

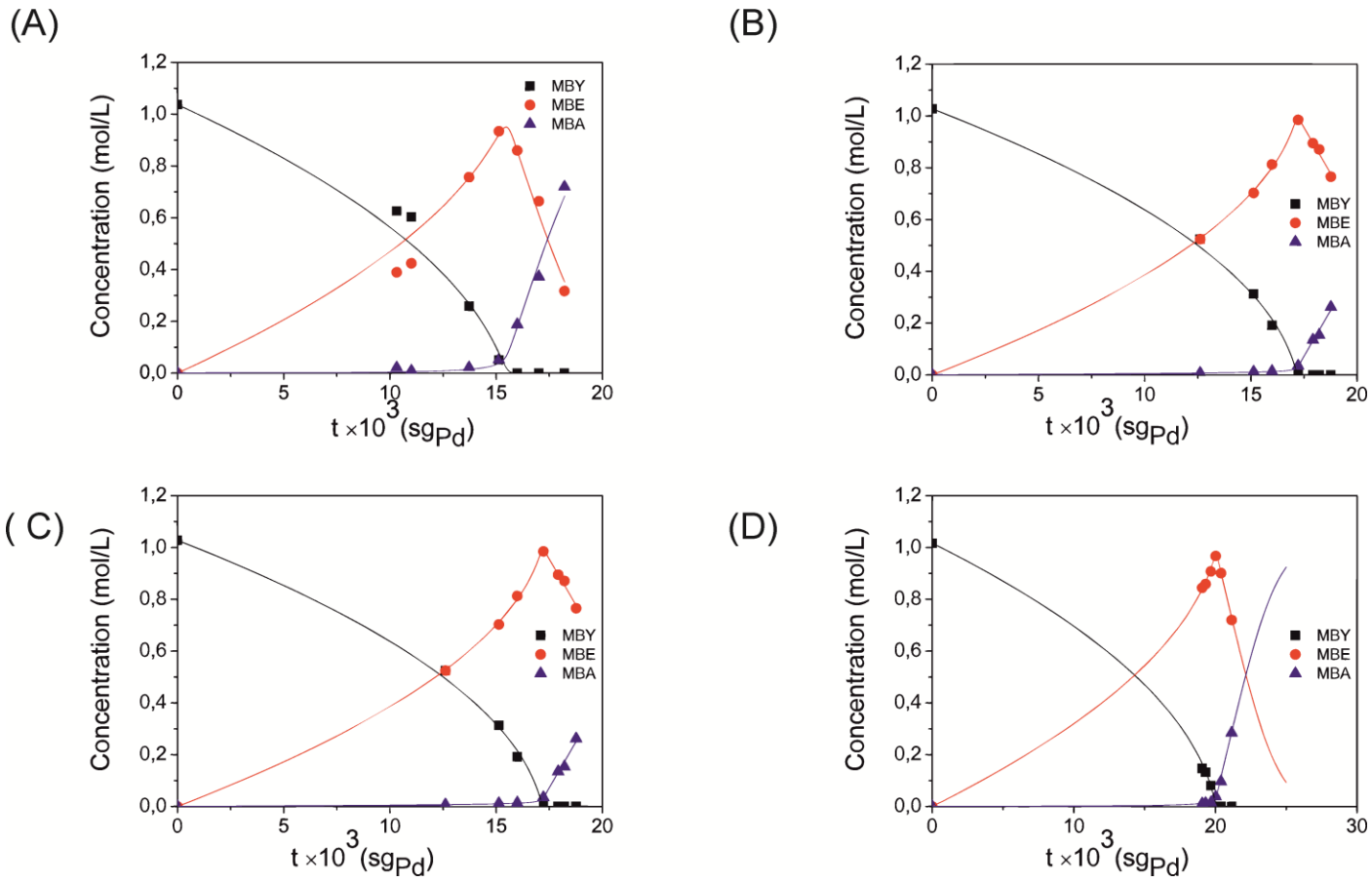

Figure S6. Dependences of the concentrations of MBY, MBE and MBA on the contact time after different pretreatments on PdZn/$Ti_{0.95}Ce_{0.05}O_2$ -a (A), PdZn/$Ti_{0.95}Ce_{0.05}O_2$ -b (B), PdZn/ $Ti_{0.95}Ce_{0.05}O_2$ - c (C), PdZn/$Ti_{0.95}Ce_{0.05}O_2$ -d (D), points - experiment, lines - calculation by the Langmuir-Hinshelwood model. Reaction conditions: gas flow rate 6.0 mL/min, = 1 atm, T = 313 K.

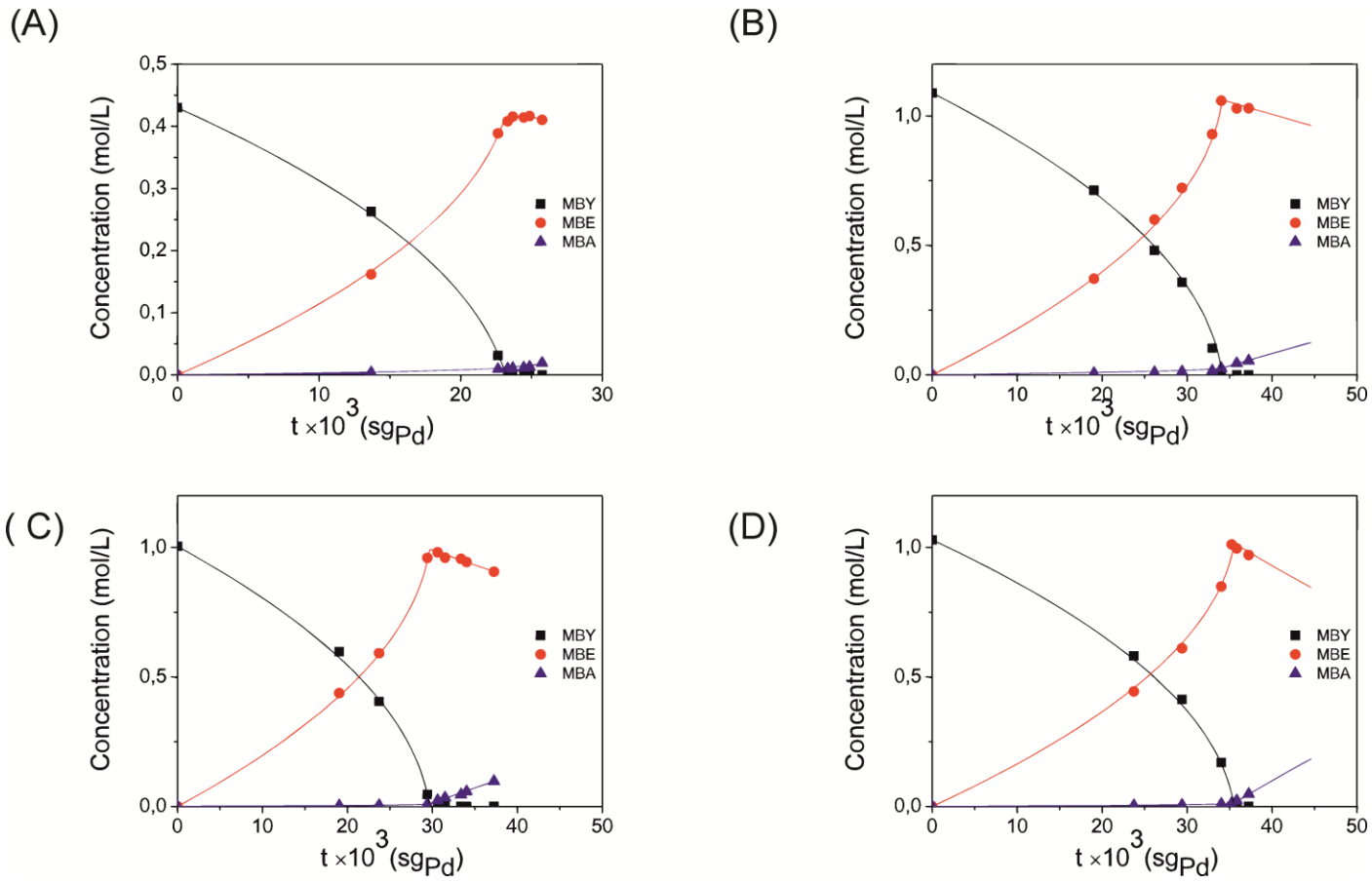

Figure S7. Dependences of the concentrations of MBY, MBE and MBA on the contact time after different pretreatments on PdZn/$Ti_{0.8}Zn_{0.2}O_2$ -a (A), PdZn/$Ti_{0.8}Zn_{0.2}O_2$ -b (B), PdZn/$Ti_{0.8}Zn_{0.2}O_2$ -c (C), PdZn/$Ti_{0.8}Zn_{0.2}O_2$ -d (D), points - experiment, lines - calculation by the Langmuir-Hinshelwood model. Reaction conditions: gas flow rate 6.0 mL/min, = 1 atm, T = 313 K.

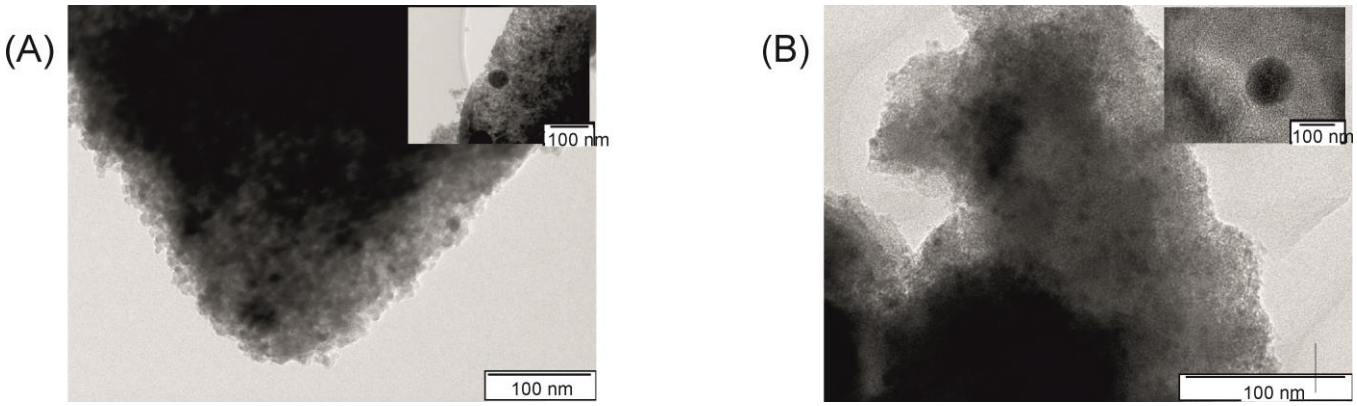

Figure S8. TEM micrographs of the powdered catalysts (A) PdZn/TiO_2-d, (B) PdZn/$Ti_{0.95}Ce_{0.05}O_2$-d.

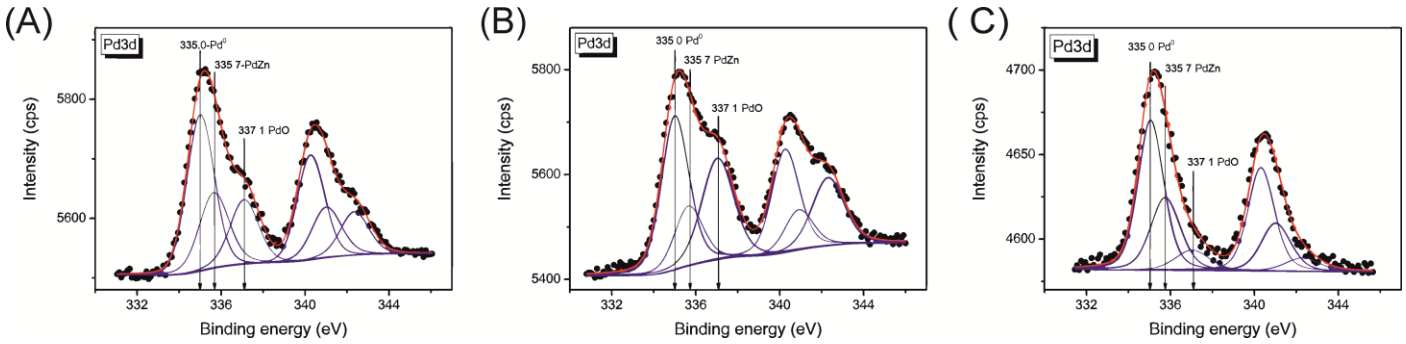

Figure S9. Peak fitting of $Pd3d_{5/2}$ core-level spectra of (A) $PdZn/TiO_2$-d, (B) $PdZn/Ti_{0.95}Ce_{0.05}O_2$-d, and (C) $PdZn/Ti_{0.8}Zn_{0.2}O_{1.8}$-d after calcination at 573 K in air and reduction with 30 vol.% hydrogen in argon at 573 K for 2 h.