Dual-cycle mechanism based kinetic model for DME-to-olefin synthesis on HZSM-5-type catalysts.

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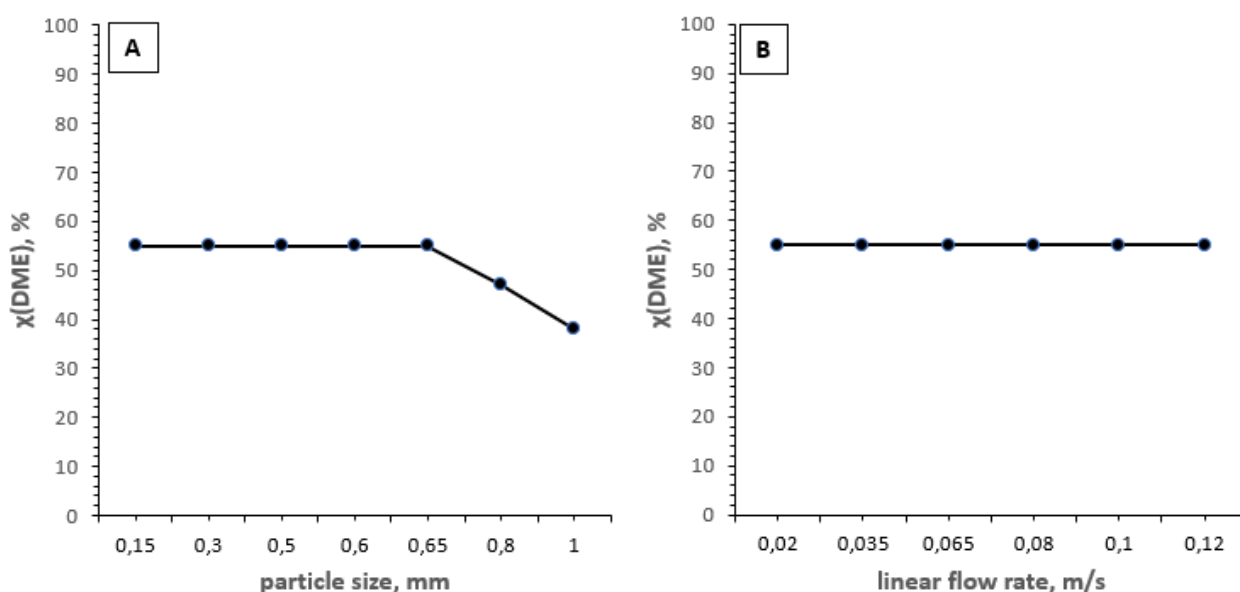*Correspondence: av-star@ips.ac.ru; Tel.: +79267032733

Figure S1. Dependence of DME conversion on the catalyst particle size (**A**) and linear flow rate (**B**). T = 320°C. Catalyst Mg-HZSM-5 / Al_2O_3.

Table S1. Reactions and equations of reaction rates.

	№	Reaction	Reaction rates equations
Interconversion of hydrocarbon pool intermediates	1.	$CP + ZH \rightarrow 2\ C_3H_6$	$r_1 = k_1$
	2.	$2\ C_3H_6 \rightarrow CP + ZH$	$r_2 = k_2 \cdot C(C_3H_6)^2$
Olefins methylation	3.	$C_2H_4 + DME \rightarrow C_3H_6 + MeOH$	$r_3 = k_3 \cdot C(C_2H_4) \cdot C(DME)$
	4.	$C_2H_4 + MeOH \rightarrow C_3H_6 + H_2O$	$r_4 = k_4 \cdot C(C_2H_4) \cdot C(MeOH)$
	5.	$C_3H_6 + DME \rightarrow C_4H_8 + MeOH$	$r_5 = k_5 \cdot C(C_3H_5) \cdot C(DME)$
	6.	$C_3H_6 + MeOH \rightarrow C_4H_8 + H_2O$	$r_6 = k_6 \cdot C(C_3H_6) \cdot C(MeOH)$
	7.	$C_4H_8 + DME \rightarrow C_5H_{10} + MeOH$	$r_7 = k_7 \cdot C(C_4H_{78}) \cdot C(DME)$
	8.	$C_4H_8 + MeOH \rightarrow C_5H_{10} + H_2O$	$r_8 = k_8 \cdot C(C_4H_8) \cdot C(MeOH)$
	9.	$C_5H_{10} + DME \rightarrow C_6H_{12} + MeOH$	$r_9 = k_9 \cdot C(C_5H_{910}) \cdot C(DME)$
	10.	$C_5H_{10} + MeOH \rightarrow C_6H_{12} + H_2O$	$r_{10} = k_{10} \cdot C(C_5H_{10}) \cdot C(MeOH)$
Olefins dimerization, cracking	11.	$C_6H_{12} \rightarrow 2\ C_3H_6$	$r_{11} = k_{11} \cdot C(C_6H_{12})$
	12.	$2\ C_3H_6 \rightarrow C_6H_{12}$	$r_{12} = k_{12} \cdot C(C_3H_6)^2$
	13.	$C_6H_{12} \rightarrow C_2H_4 + C_4H_8$	$r_{13} = k_{13} \cdot C(C_6H_{12})$
Interconversion of hydrocarbon pool intermediates	14.	$C_6H_{12} \rightarrow CP + ZH$	$r_{14} = k_{14} \cdot C(C_6H_{12})$
	15.	$CP \rightarrow C_6 + 5\ ZH$	$r_{15} = k_{15}$
	16.	$C_6 + 5ZH \rightarrow CP$	$r_{16} = k_{16}$
Aromatics methylation	17.	$C_6 + 2\ DME \rightarrow C_8 + 2\ MeOH$	$r_{17} = k_{17} \cdot C(DME)^{\alpha_{17-18}}$
	18.	$C_6 + 2\ MeOH \rightarrow C_8 + 2\ H_2O$	$r_{18} = k_{18} \cdot C(MeOH)^{\alpha_{17-18}}$
Aromatics formation Dealkylation of aromatic intermediates	19.	$C_8 \rightarrow C_8H_{10}$	$r_{19} = k_{19}$
	20.	$C_8H_{10} + 4ZH \rightarrow 2\ CH_4 + C_6$	$r_{20} = k_{20}$
	21.	$C_8 \rightarrow C_6 + C_2H_4$	$r_{21} = k_{21}$
Reversible reaction of DME hydration	22.	$DME + H_2O \rightarrow 2\ MeOH$	$r_{22} = k_{22} \cdot C(DME) \cdot C(H_2O)$
	23.	$2\ MeOH \rightarrow DME + H_2O$	$r_{23} = k_{23} \cdot C(MeOH)^2$
Alkanes formation	24.	$C_2H_4 + 2\ ZH \rightarrow C_2H_6$	$r_{24} = k_{24} \cdot C(C_2H_4)^{\alpha_{24}}$
	25.	$C_3H_6 + 2\ ZH \rightarrow C_3H_8$	$r_{25} = k_{25} \cdot C(C_3H_6)^{\alpha_{25}}$
	26.	$C_4H_8 + 2\ ZH \rightarrow C_4H_{10}$	$r_{26} = k_{26} \cdot C(C_4H_8)^{\alpha_{26}}$
	27.	$C_5H_{10} + 2\ ZH \rightarrow C_5H_{12}$	$r_{27} = k_{27} \cdot C(C_5H_{10})^{\alpha_{27}}$

Table S2. Reaction orders with respect to the component.

	Component	Mg-HZSM-5 / Al₂O₃	HZSM-5 / Al₂O₃	Zr-HZSM-5 / Al₂O₃
α_{17-18}	DME/MeOH	1.98	2.00	1.49
α_{24}	C_2H_4	0.00	0.27	0.09
α_{25}	C_3H_6	1.39	1.38	1.29
α_{26}	C_4H_8	0.86	1.20	1.16
α_{27}	C_5H_{10}	0.54	0.43	0.59

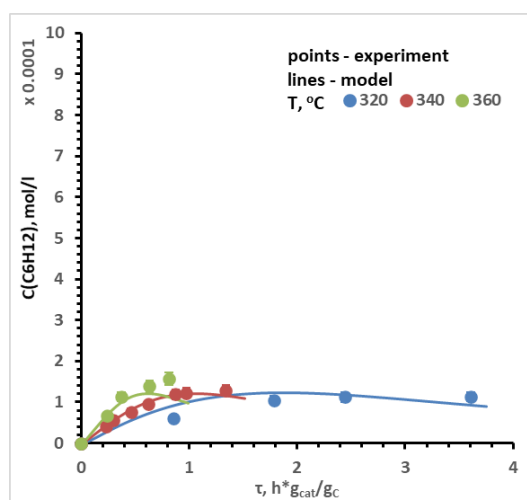**Figure S2.** Calculated and experimental dependencies of the hexenes concentrations on specified contact time at T = 320-360°C. Catalyst Mg-HZSM-5 / Al₂O₃.
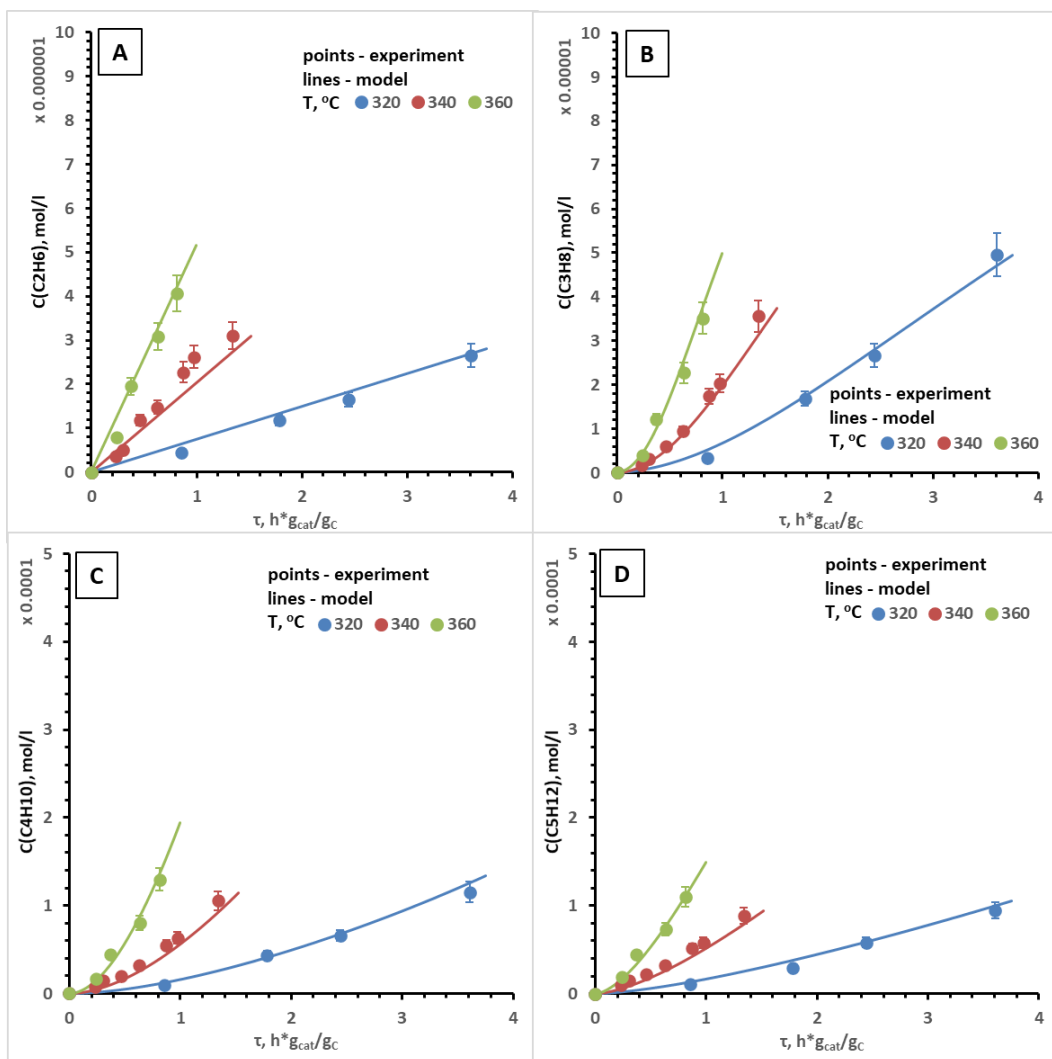
Figure S3. Calculated and experimental dependencies of the concentrations of Ethane **(A)**, Propane **(B)**, Butanes **(C)**, Pentanes **(D)** on specified contact time at T = 320-360°C. Catalyst Mg-HZSM-5 / Al_2O_3.
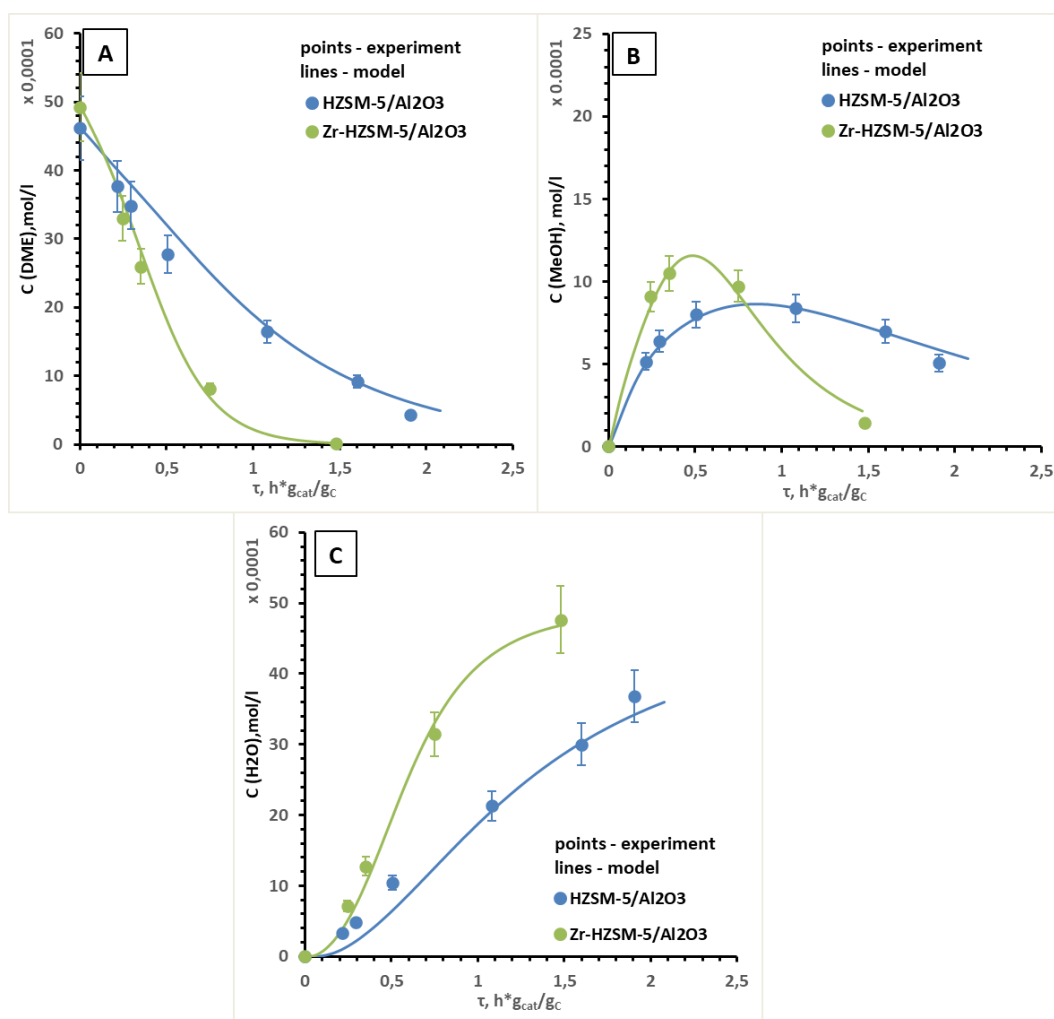
Figure S4. Calculated and experimental dependencies of the concentrations of DME **(A)**, Methanol **(B)**, and Water **(C)** on specified contact time at T = 320°C. Catalysts HZSM-5 / Al$_2$O$_3$ and Zr-HZSM-5 / Al$_2$O$_3$.
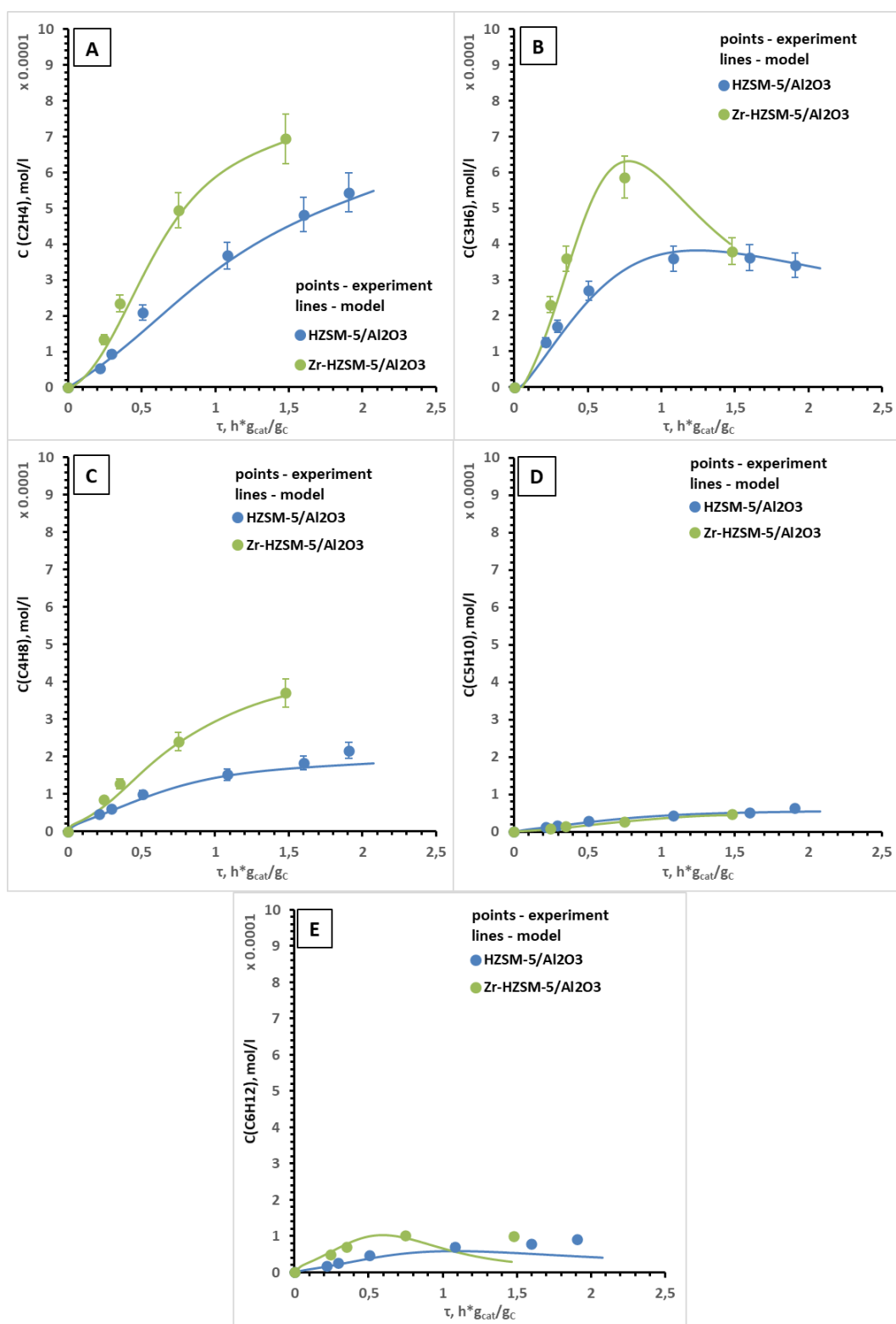
Figure S5. Calculated and experimental dependencies of the concentrations of Ethylene **(A)**, Propylene **(B)**, Butenes **(C)**, Pentenes **(D)** and Hexenes **(E)** on specified contact time at T = 320°C. Catalysts HZSM-5 / Al_2O_3 and Zr-HZSM-5 / Al_2O_3.
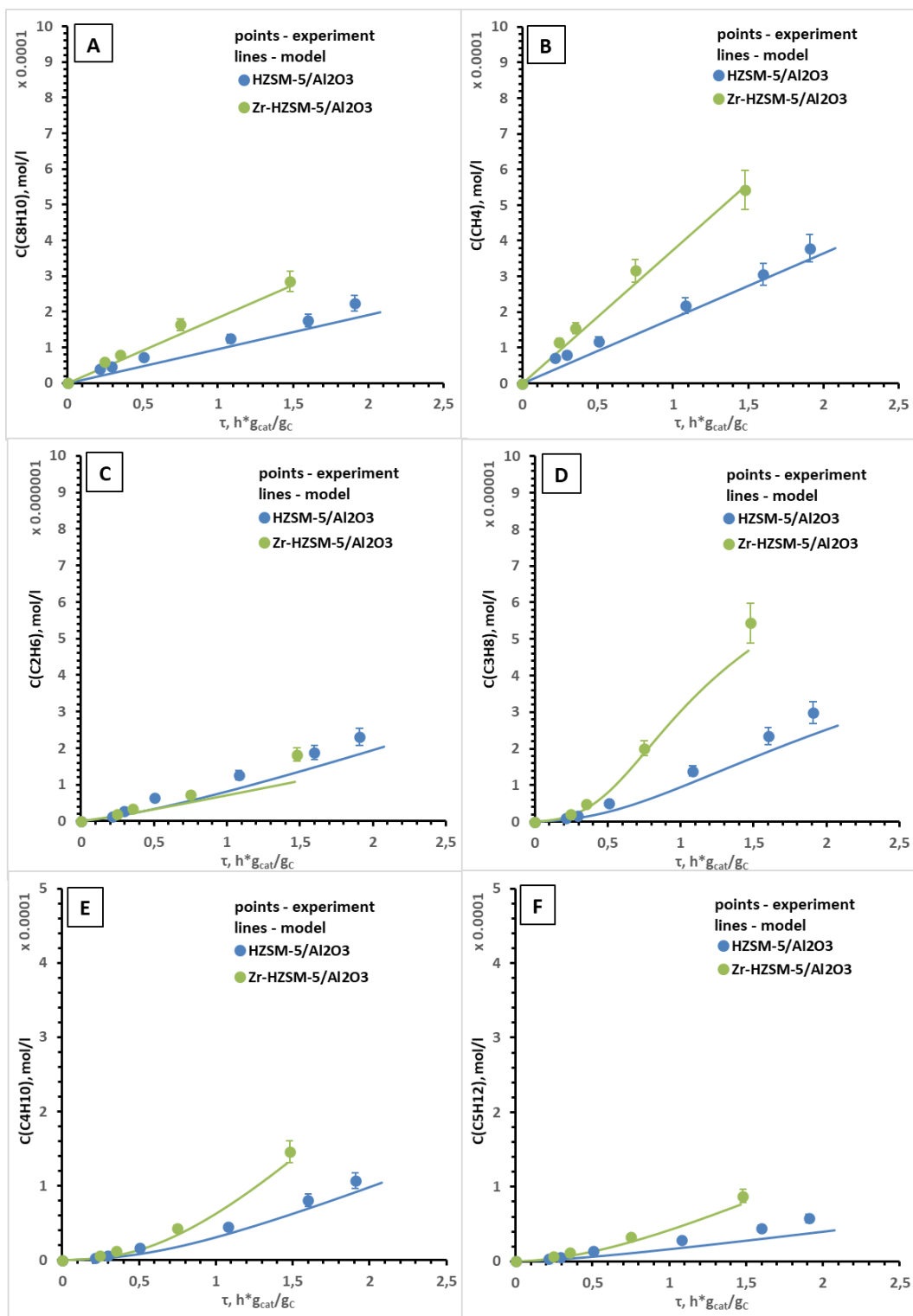
Figure S6. Calculated and experimental dependencies of the concentrations of Ethylene Aromatics C_8H_{10} **(A)**, Methane **(B)**, Ethane **(C)**, Propane **(D)**, Butane **(E)**, and Pentane **(F)** on specified contact time at T = 320°C. Catalysts HZSM-5 / Al_2O_3 and Zr-HZSM-5 / Al_2O_3.
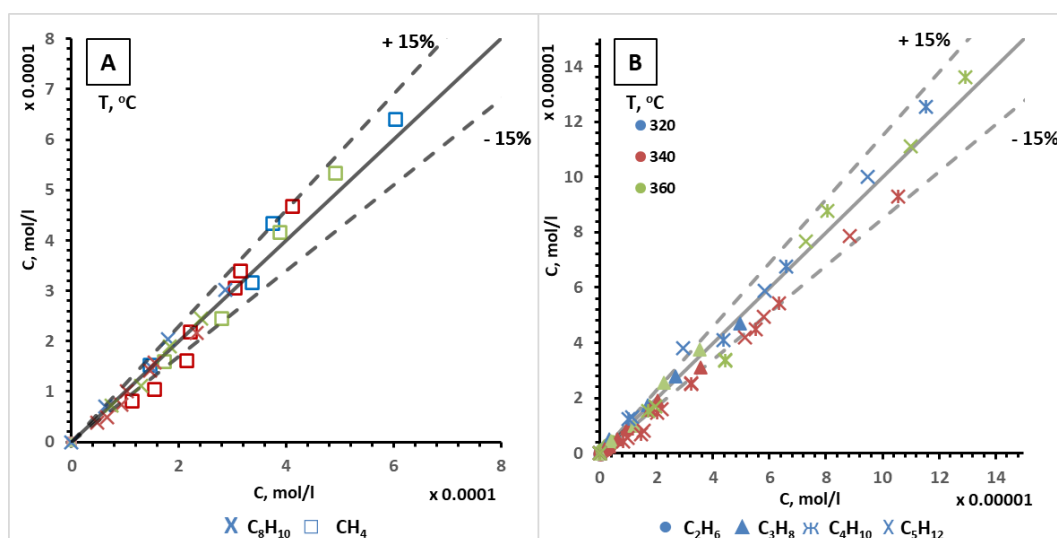
Figure S7. Correlation of calculated and experimental concentrations of Aromatics C_8H_{10} and Methane **(A)**, Alkanes C_2-C_5 **(B)**. T = 320-360°C. Catalyst Mg-HZSM-5 / Al_2O_3.
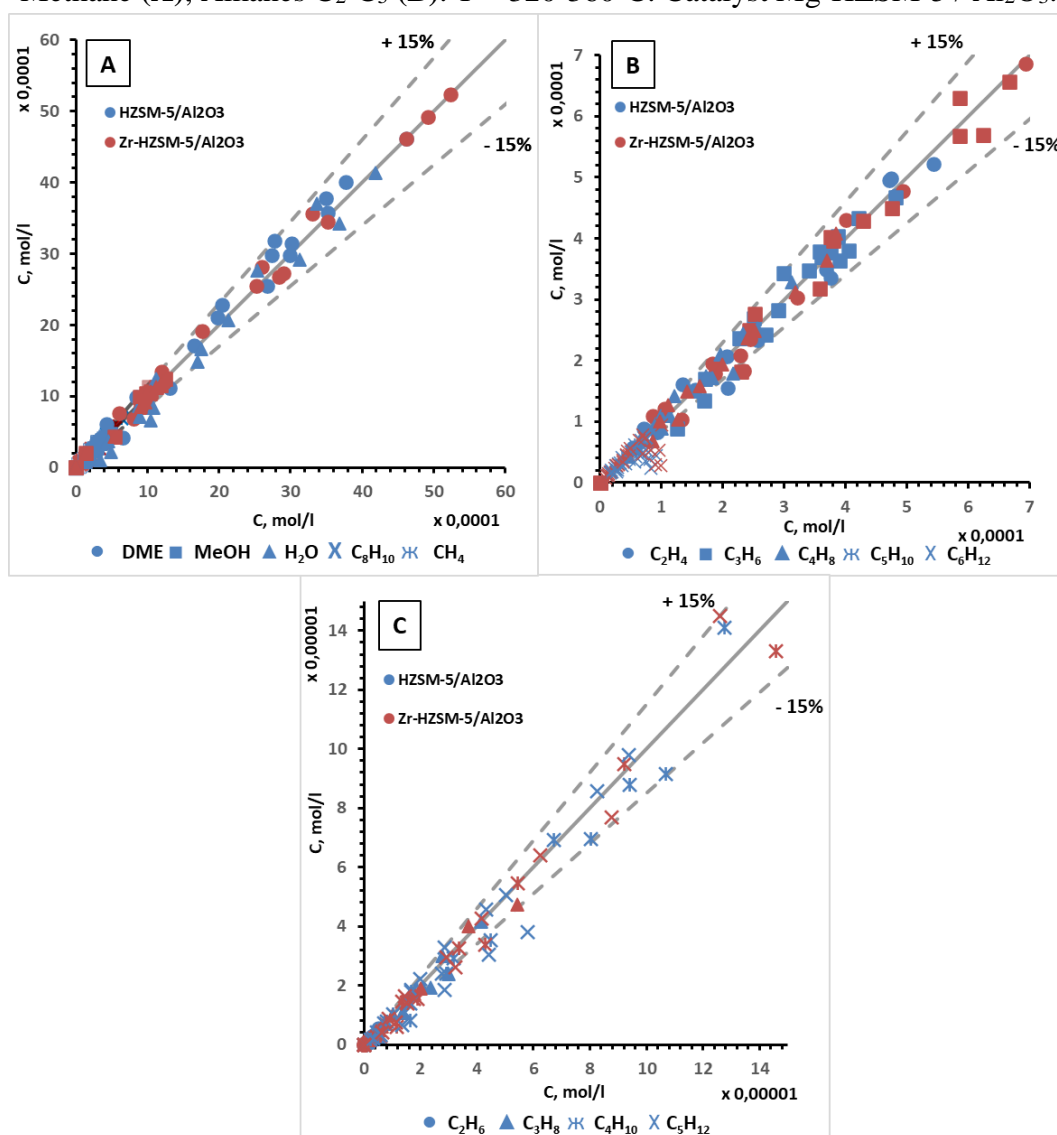

Figure S8. Correlation of calculated and experimental concentrations of Oxygenates, aromatic compounds C_8H_{10} and Methane (A), Olefins C_2-C_6 (B), Alkanes C_2-C_5 (C). T = 320-360°C. Catalysts HZSM-5 / Al_2O_3 and Zr-HZSM-5 / Al_2O_3.

Table S3. Variance Analysis for the Kinetic Model.

Criterea	Mg-HZSM-5 / Al$_2$O$_3$	HZSM-5 / Al$_2$O$_3$	Zr-HZSM-5 / Al$_2$O$_3$
φ_f	$7.28 \cdot 10^{-7}$	$1.44 \cdot 10^{-6}$	$6.58 \cdot 10^{-7}$
ν_f	139	181	111
S_f	$5.2 \cdot 10^{-9}$	$8.0 \cdot 10^{-9}$	$5.9 \cdot 10^{-9}$
φ_e*	$3.7 \cdot 10^{-6}$	$4.6 \cdot 10^{-6}$	$3.1 \cdot 10^{-6}$
ν_e*	392	476	336
S_e	$9.4 \cdot 10^{-9}$	$9.6 \cdot 10^{-9}$	$9.2 \cdot 10^{-9}$
S_f/S_e	0.55	0.83	0.64
$F_{0.05}(\nu_f,\nu_e)$	1.25	1.21	1.28
significance test	valid	valid	valid

*every experiment was repeated 2-4 times