catalysts

Supplementary Data belonging to:

Investigations on the ethylene polymerization with bisarylimine pyridine iron (BIP) catalysts

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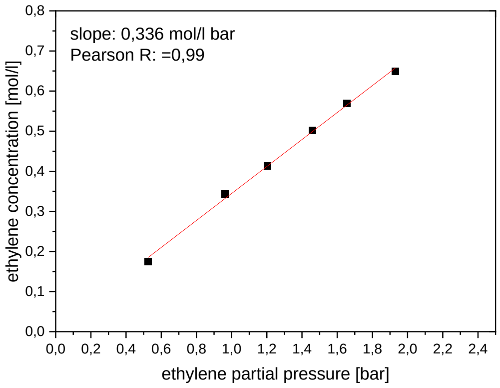

Figure S1. Plot of ethylene dissolved in 300 mL of toluene with 45 mmol/l MAO at various ethylene partial pressures at 15 °C.

The amount of gaseous ethylene in the reactor (n_{gas}) was calculated by using the viral form of the Van der Waals equation. The measured ethylene concentration as a function of the ethene partial pressure yields a straight line with a slope of 0.336 as Henry constant.[1,2]

1. Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed., Prentice Hall: New Jersey, 1999, 712 ff.
2. Dornik, H. P. Deaktivierungskinetik metallocenkatalysierter Ethenpolymerisationen, Dissertation, Technische Universität Darmstadt, Darmstadt, 2003.

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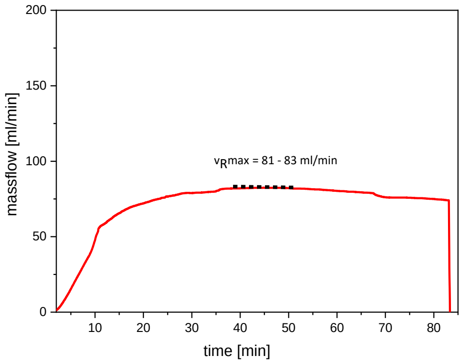

Figure S2. Time dependent ethene volume flow during the polymerization mediated by catalyst **1** (45 mmol/L Al (MAO), 0.33 µmol/L of **1**, 15 °C, 2 bar of ethene pressure).

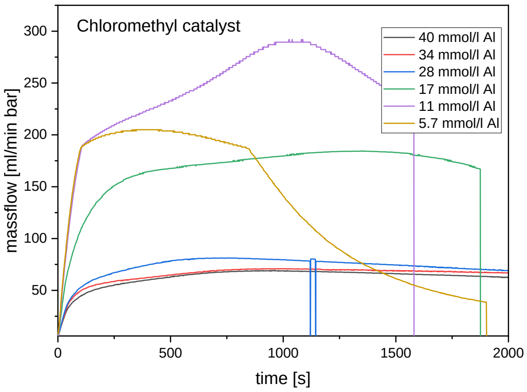

Figure S3. Ethylene massflow (normalized to 1 bar ethene) at varying aluminum concentrations during polymerization catalysis by **4**. Reaction conditions: 0.8 µmol/L catalyst, 10 °C, 2 bars of ethylene.

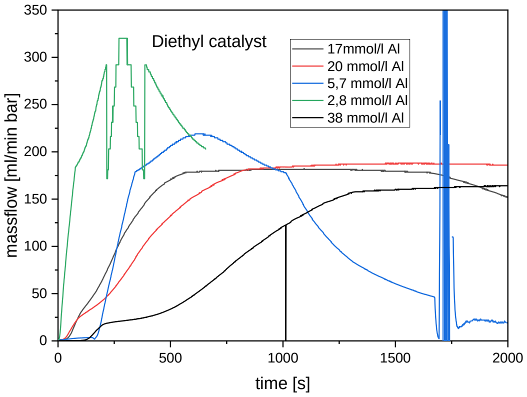

Figure S4. Ethylene massflow (normalized to 1 bar ethene) at varying aluminum concentrations during polymerization catalysis by **2**. The spikes at 2.8 mmol/L Al result from a temporary technical problem with the massflow controller. Reaction conditions: 0.6 µmol/L catalyst, 10 °C, 2 bars of ethylene.

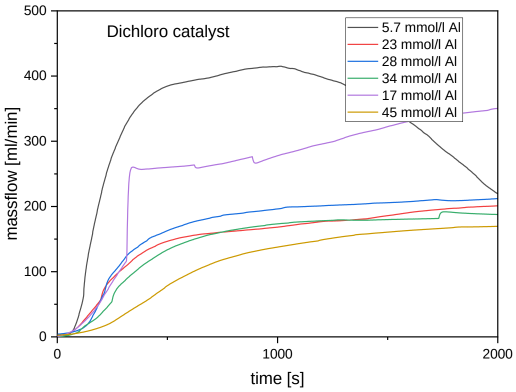

Figure S5. Ethylene massflow at varying aluminum concentrations during polymerization catalysis by **1**. Reaction conditions: 0.6 µmol/L catalyst, 15 °C, 2 bars of ethylene.

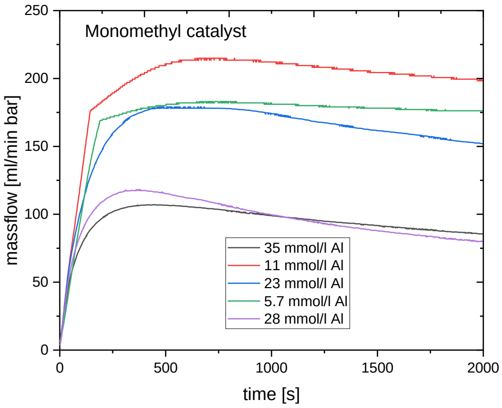

Figure S6. Ethylene massflow (normalized to 1 bar ethene) at varying aluminum concentrations during polymerization catalysis by **5**. Reaction conditions: 0.5 µmol/L catalyst, 10 °C, 2 bars of ethylene.

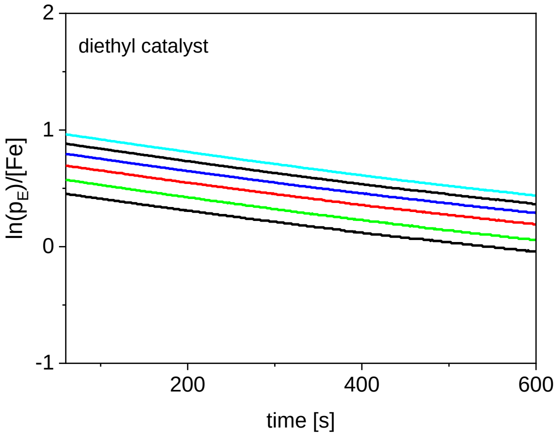

Figure S7. Normalized logarithmic ethylene pressure loss against the reaction time for catalyst **2.** Reaction conditions: 0.5 µmol/L catalyst, 40 mmol/L of MAO, 5 °C, 1-3 bar ethylene.

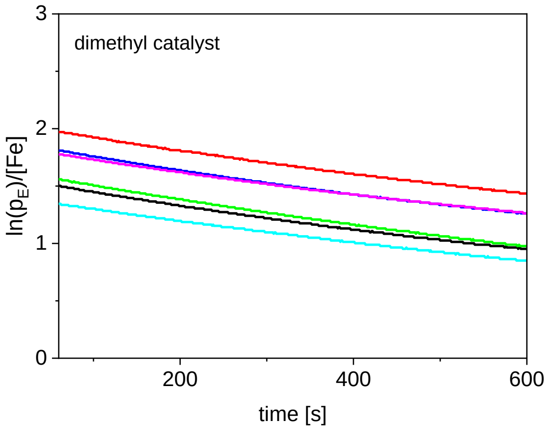

Figure S8. Normalized logarithmic ethylene pressure loss against the reaction time for catalyst **3.** Reaction conditions: 0.5 µmol/L catalyst, 40 mmol/L of MAO, 5 °C, 1-3 bar ethylene.

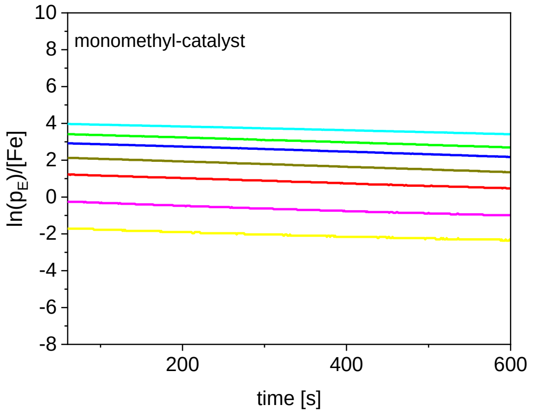

Figure S9. Normalized logarithmic ethylene pressure loss against the reaction time for catalyst **5.** Reaction conditions: 0.3 µmol/L catalyst, 40 mmol/L of MAO, 5 °C, 1-3 bar ethylene.

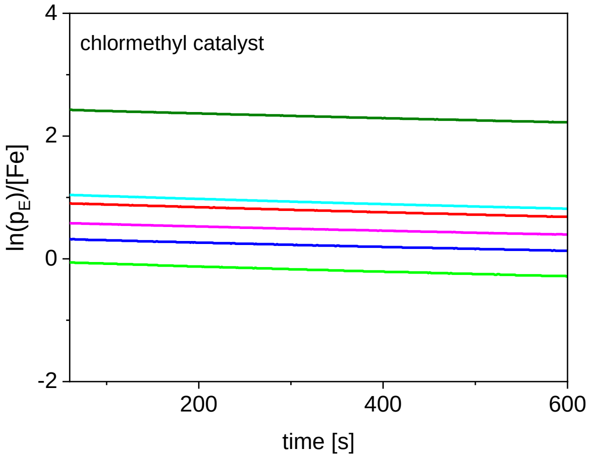

Figure S10. Normalized logarithmic ethylene pressure loss against the reaction time for catalyst **4.** Reaction conditions: 0.8 µmol/L catalyst, 40 mmol/L of MAO, 5 °C, 1-3 bar ethylene.

Table S1. Slopes of the regression lines of the respective kinetic studies with confidence interval. k' is normalized to 1 mol/L catalyst. For reaction conditions see description of respective figure (Figure 4-6, S7-S10).

catalyst	order of Fe	order of Al	k´ [s^{-1}]
1	1.00 +/- 7.5 10^{-16}	-1,09 +/- 0.1	650 +/- 20
	-	-	380 +/- 40
2	1.06 +/- 1.45 10^{-15}	-1,03 +/- 0.16	1890+/- 50
3	1.09 +/- 6.8 10^{-16}	-0,79 +/- 0.05	980+/- 40
4	1.00 +/- 0.05	-0.80 +/- 0.17	350 +/- 30
5	1.02 +/- 3.7 10^{-16}	0.78 +/- 0.19	1350+/- 70

Mathematical derivation of the kinetics and determination of the reaction orders

The general rate law for the chain propagation of the ethylene polymerization is given by:

$$r_p = -\frac{d[M]}{dt} = k_P\ [M]^a\ [Fe]^{b}_{active}\ [Al]^c \quad [\text{mol/L s}] \qquad \text{(S1)}$$

k_p: rate constant of chain propagation $\left[\frac{L^{a+b+c-1}}{s\ mol^{a+b+c-1}}\right]$
[M]: monomer concentration [mol/L]
$[Fe]_{active}$: concentration of active catalyst [mol/L]
[Al]: concentration of cocatalyst [mol/L]

The reaction order with respect to the monomer was determined, using a combination of the flooding and integral method. The rate law can be integrated over time by setting a rate constant *k*′ including the concentrations of the aluminum and activated iron. The method assumes that the concentration of aluminum and active catalyst is constant which is the case after reaching the activity maximum at high MAO concentrations. The integrated first order rate law of the ethylene polymerization with respect to the monomer is defined as:

$$\ln\frac{[M]_t}{[M]_0} = k'\ t \qquad \text{(S2)}$$

$$k' = k_P\ [Fe]^{b}_{aktiv}[Al]^c \qquad \text{(S3)}$$

Within the scope of *Henrys law*, the ethylene concentration is proportional to the partial pressure of the ethylene (if *T*, *V* is constant). If the ethylene pressure is within this range, the monitored partial ethylene pressure can be used. The pressure dependent first order rate law is given by:

$$\ln\frac{p_t}{p_0} = -k'\ t \qquad \text{(S5)}$$

To identify the reaction order of the ethylene polymerization, the rate constants of various reactions with different initial pressures were determined according to equation S5. Plotting the monitored pressure p_t/p_0 on a logarithmic scale give lines with the slope of *k*′.

The dependency of the chain propagation on the iron and aluminum concentration can be analysed by semi batch experiments at constant ethylene pressure applying the method of flooding. The reaction rate is directly related to the monitored ethylene consumption and is given by:

$$r_p = k'' \, [Al]^c \, [Fe]^{b}_{active} \qquad (S6)$$

$$k'' = k_p \, [M]^a \qquad (S7)$$

To determine the reaction order of either iron or aluminum, the concentration of the other compound was held constant. Plotting the reaction rate against the varying concentration of one of the compounds in a double logarithmic scale gives a straight line with a slope of the order of reaction.

For a Cossee-Arlman mechanism for the propagation step the general rate law for the chain propagation is:

$$r_p = k_p \, [Fe]_{active} \, [E] \qquad (S8)$$

The precatalyst (L_nFeCl_2) is alkylated by the aluminum compound AlR_3 (once or twice) leading an alkylated bimetallic compound:

$$L_nFeCl_2 + 3\ AlR_3/MAO \rightarrow L_nFe^+R—AlR_3 \bullet AlR_3Cl^- (/MAOCl^-) + AlR_2Cl$$

The iron-aluminum compound leads to an active catalyst species in a chemical equilibrium: $L_nFe^+\mathrm{R}—\mathrm{Al}R_3 \rightleftarrows L_nFe^*\mathrm{R} + \mathrm{Al}R_3$

$$K = \frac{[L_nFe^*\mathrm{R}]\,[\mathrm{Al}R_3]}{[L_nFe^+\mathrm{R}—\mathrm{Al}R_3]} \qquad (S9)$$

It can be assumed that K is small in a toluene solution, and thus that $[L_nFe^+\mathrm{R}—\mathrm{Al}R_3] \approx L_nFeCl_2 = [Fe]_0$. The concentration of active catalyst ($[L_nFe^*\mathrm{R}] = [Fe^+]$) is than proportional to $[Fe]_0$:

$$[Fe^+] = \frac{K[Fe]_0}{[AlR_3]} \qquad (S10)$$

Substitution of S10 into S8 gives for the initial reaction rate:

$$r_{p,i} = K * k_p \frac{[Fe]_0[E]}{[AlR_3]} \qquad (S11)$$