Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Supporting Information

Dimerization of ethene in a fluidized bed reactor using Ni-based Supported Ionic Liquid Phase (SILP) catalysts

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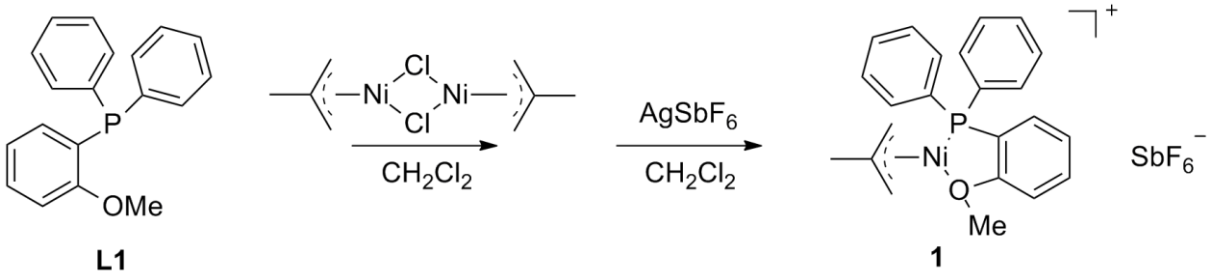
Synthesis of the nickel complexes

*Preparation of Ni complex [(mall)Ni-dppanis][SbF_6] **1***

The synthesis was carried out according to a modified procedure of Heinicke et al.[Ref. 36 b)] A solution of phosphine ligand S1 (876 mg, 3.0 mmol) in CH_2Cl_2 (15 mL) was added to the red solution of (methallylNiBr)$_2$ S2 (580 mg, 1.50 mmol) in CH_2Cl_2 (15 mL) and stirred for 1 h at about 20 °C. The resulting orange solution was added to a suspension of $AgSbF_6$ (1.035 g, 3.0 mmol) in CH_2Cl_2 (15 mL), stirred for 10 min, and filtered after cooling to -20 °C. The solvent of the filtrate was removed in a vacuum, and the residue was crystallized from CH_2Cl_2/hexane.



Scheme S1. *Synthesis of of Ni complex [(mall)Ni-dppanis][SbF_6] **1**.*

Pressure drop curves

The pressure drop curves were recorded within a 15 mm glass reactor. Therefore 5 or 2.5 g of the support material was fluidized with a nitrogen or argon carrier flow. The pressure drop over the particles was recorded with a GDH digital precision manometer (0-199.9 mbar) with a resolution of 0.1 mbar or a U-tube manometer with a maximum resolution of 0.05 mbar.

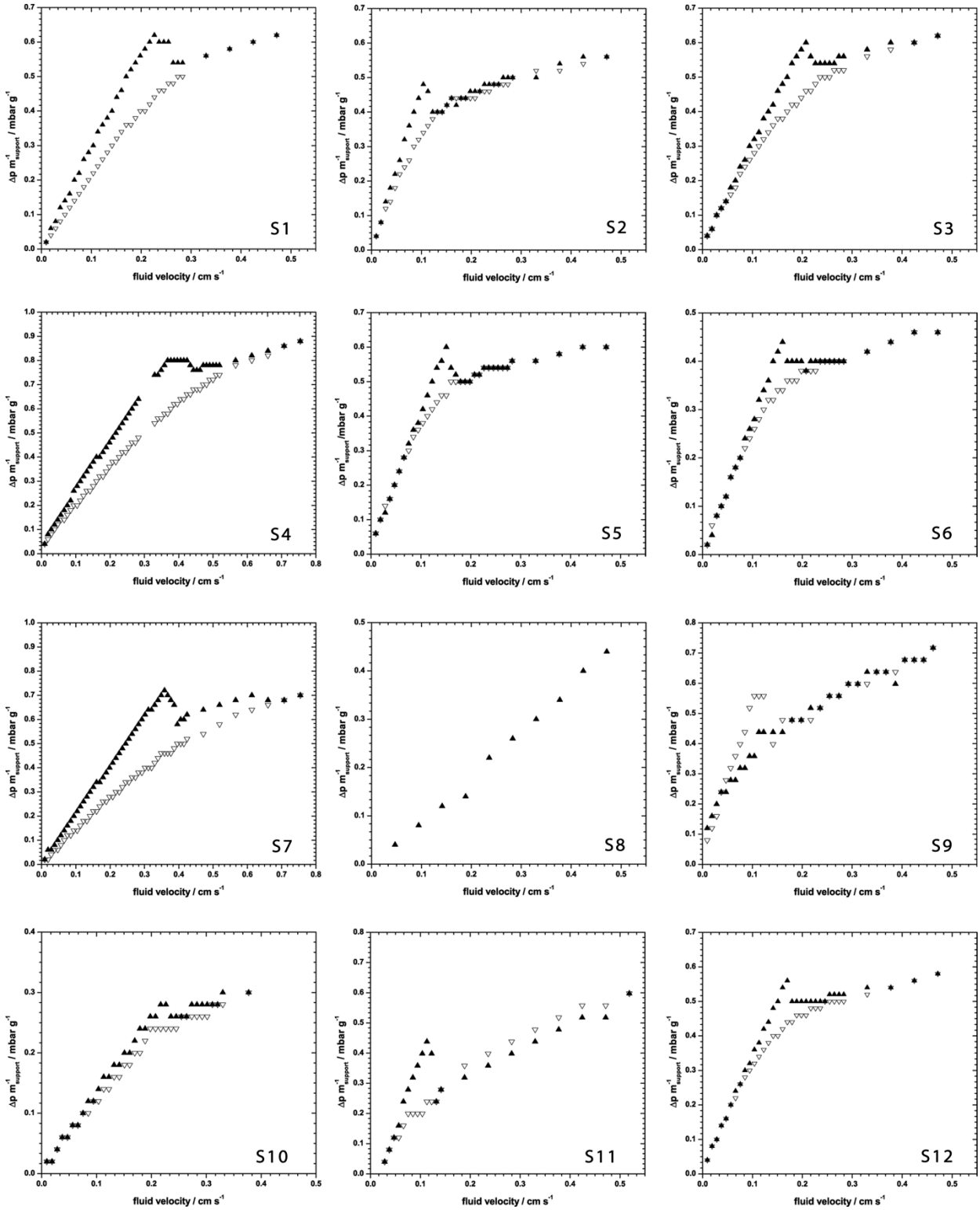


Figure S1. *Pressure drop of different support materials S1-S12 with increasing (⌣) and decreasing (⌢) nitrogen volume flow; d_i = 15 mm, p = 1 bar, T = 293 K.*

Prediction of minimum fluidization velocity

The Reynolds number at minimum fluidization conditions was calculated according to eq. 9, as it is reported in the literature [36,37].

$$\mathrm{Re}_{mf} = \left(138{,}24^2 + 0{,}0605 Ar\right)^{0{,}5} - 138{,}24\right) \qquad (9)$$

Catalytic experiments

In preliminary studies we replicate the reaction parameters of our previos studies of Ni-dppanis based SILP-catalysts in a fixed-bed reactor [12] within the fluidized bed reactor. Therefore, the reaction was conduced with pure ethene. Since this lead to an enormous temperature rise inside the catalytic bed we consequently diluted the feed with nitrogen. Though this resulted in a delayed reactivity of the SILP catalysts the observable deactivation was still undesired (compare Figure S2).

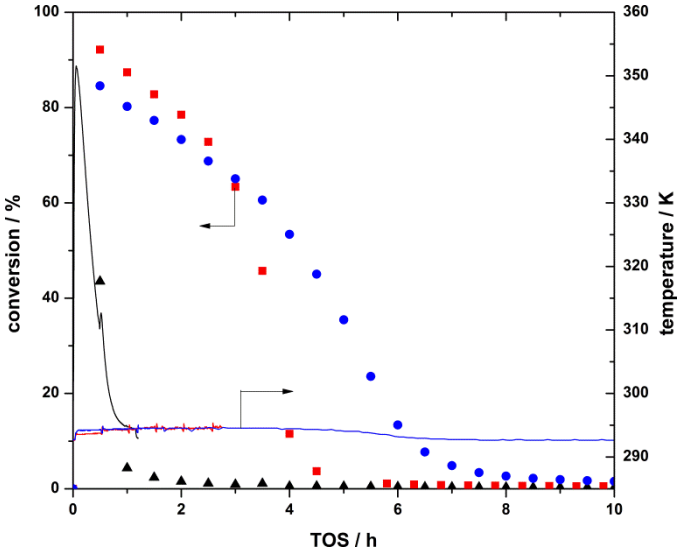


Figure S2. *Conversion of ethene and temperature inside the fluidized bed over time on stream with 100 vol.-%* (‿), *50 vol.-%* ( ) *and 10 vol.-%* ( ) *of ethene in a nitrogen stream (both not purified); d_i = 10 mm, p = 1 bar, T = 292 K; SILP catalysts with Ni-dppanis complex, w_{Ni} = 2.50 mg_{Ni} $g_{support}^{-1}$,* ***S7****, [C_2C_1Im][FAP], a_{IL} = 0.3; m_{SILP} = 1000 mg, V_{total} = 51 Nml min^{-1}, t ≈ 2 s, $p_{reaction}$ = 1 bar.*

With a different batch of Ni-dppanis precursor we also applied a reaction temperature of 272 K in the fluidized bed, as it is shown in Figure S3. Althought there was a smaller initial effective raction rate observable, the deactivation coefficient for a second order deactivation and the calculated deactivation course fits very well our data recorded for the temperatures of 282, 292 and 302 K. Hence the measured deactication ceofficient $k_{d,2} = 1.64 \cdot 10^{-6}$ m^3 mol^{-1} was also taken into account for the calculation of the activation energy of deactivation depicted in Figure 9.

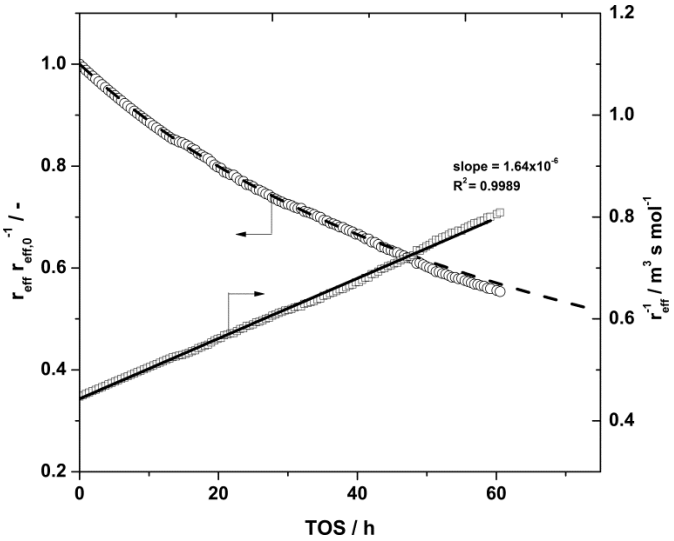


Figure S3. *Measured ( ) and calculated (dashed line) deactivation for SILP-catalyst applied in the fluidized bed at 272 K and linearization (solid line) of 2nd order deactivation by plotting* r_{eff}^{-1} *over time on stream ( ) for Ni-dppanis complex,* w_{Ni} *= 2.50* mg_{Ni} $g_{support}^{-1}$, ***S7***, $[C_2C_1Im][FAP]$, a_{IL} *= 0.3;* m_{SILP} *= 200 mg,* p_{ethene} *= 68 mbar,* V_{ethene} *= 5.1 Nml* min^{-1}, $t \approx 0.3$ *s,* $p_{reaction}$ *= 1 bar.*