Electronic supplementary information (ESI)

The Effect of MoO_X structure on the reaction pathways of propene formation in the metathesis of ethylene and 2-butene

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Experimental details

For calculating conversion and selectivity, *cis*-2-butene was not considered as a product. The Mo-related reaction rate (r_{Mo}) of propene formation and ethylene consumption was calculated according to equation (1) and (2), respectively. The selectivity (S) to compound i and the conversion of 2-butene were calculated using equation (3) und (4), respectively.

$$r_{Mo}\left[\frac{\text{molecule}_{\text{propene}}}{\text{Mo}-\text{atome}\cdot\text{s}}\right]=\frac{x_{\text{propene}}\cdot\dot{V}_F\cdot N_A}{S_{BET}\cdot m_{\text{catalyst}}\cdot V_M\cdot\omega_{Mo}} \quad (1)$$

$$r_{Mo}\left[\frac{\text{molecule}_{\text{ethylene}}}{\text{Mo}-\text{atome}\cdot\text{s}}\right]=\frac{X_{\text{ethylene}}\cdot x_{\text{ethylene},0}\cdot\dot{V}_F\cdot N_A}{S_{BET}\cdot m_{\text{catalyst}}\cdot V_M\cdot\omega_{Mo}} \quad (2)$$

$$S_i[-]=\frac{\beta_{C,i}\cdot x_i}{(3\cdot x_{\text{propene}}+4\cdot x_{1-\text{butene}}+5\cdot x_{\text{pentene}}+6\cdot x_{\text{hexene}})} \quad (3)$$

$$X_{2-\text{butene}}[-]=1-\frac{x_{\text{trans}-2-\text{butene}}+x_{\text{cis}-2-\text{butene}}}{x_{\text{trans}-2-\text{butene},0}+x_{\text{cis}-2-\text{butene},0}} \quad (4)$$

, where X_i, x_i, $\beta_{C,i}$, $\dot{V}_F$, S_{BET}, $m_{catalyst}$, V_M, N_A and ω_{Mo} stand for conversion and mole fraction of component i, number of carbon atoms in component i, feed flow rate, catalyst specific surface area, catalyst mass, molar volume, Avogadro number and weight concentration of Mo, respectively. "0" stands for conditions at reactor inlet. Additionally, we do not distinguish the isomers of pentene and hexene.

Tables and Figures

Table ESI-1. Selectivity to propene (S) and rate of propene formation (r_{Mo}) at a conversion (X) of 2-butene in the reaction of ethylene and *trans*-2-butene with a feed composition of ethylene/*trans*-2-butene/nitrogen = 5/5/1 at 423 K and 125 kPa.

Catalyst [-]	Modified contact time [s g/ml]	X(2-butene) [-]	S(propene) [-]	r_{Mo} [s^{-1}]
0.15MoS40	0.66	0.39	0.71	0.15
0.15MoS70	0.68	0.39	0.70	0.17
1.5MoS10	0.11	0.41	0.92	0.17
1.5MoS40	0.07	0.42	0.87	0.23

Table ESI-2. Feed compositions (i) used for analysing the effect of partial pressures of ethylene and *trans*-2-butene on propene formation over 0.15MoS70 and 1.5MoS10 at 423 K and total pressure of 125 kPa.

Feed composition [-]	p(ethylene) [kPa]	p(*trans*-2-butene) [kPa]	p(nitrogen) [kPa]
(1)	0.10	0.99	0.16
(2)	0.17	0.79	0.29
(3)	0.25	0.80	0.20
(4)	0.34	0.79	0.12
(5)	0.54	0.60	0.11
(6)	0.73	0.40	0.12
(7)	0.74	0.27	0.24

Table ESI-3. Formation rate r_{BET} of products over (i) bare supports and (ii) catalysts at a conversion (X) of 2-butene in the reaction of ethylene and *trans*-2-butene with a feed composition of ethylene/*trans*-2-butene/nitrogen = 5/5/1 at 423 K and 125 kPa.

Sample [-]	X(2-butene) [-]	r_{BET}(propene) [10^{-7} mol m^{-2} s^{-1}]	r_{BET} (1-butene) [10^{-8} mol m^{-2} s^{-1}]	r_{BET} (pentene) [10^{-9} mol m^{-2} s^{-1}]
Siral10®[i]	0.10	0.00	0.94	0.46
1.5MoS10[ii]	0.10	4.04	0.00	10.9
Siral70®[i]	0.13	0.00	1.10	1.24
0.15MoS70[ii]	0.16	0.48	3.63	7.92

Table ESI-4. Rate of propene formation (r_{Mo}) and selectivity (S) at a butenes conversion (X) in the metathesis of butenes at 423 K, 125 kPa and a feed of *trans*-2-butene/1-butene/nitrogen = 5/5/1.

Catalyst [-]	Modified contact time [s g/ml]	X [-]	r_{Mo} [s^{-1}]	S(ethylene) [-]	S(propene) [-]	S(pentene) [-]	S(hexene) [-]
0.15MoS70	0.267	0.179	0.176	0.004	0.381	0.532	0.083
1.5MoS10	0.040	0.227	0.147	0.017	0.382	0.511	0.090

Table ESI-5. Rate of propene formation (r_{Mo}) in the metathesis of butenes at 423 K, 110 kPa and a feed of *trans*-2-butene and nitrogen in a ratio of 1/16.

Catalyst [-]	Modified contact time [s g/ml]	r_{Mo} [10^{-2} s^{-1}]	S(propene) [-]	S(1-butene) [-]	S(pentene) [-]
0.15MoS70	0.30	0.70	0.24	0.41	0.35
1.5MoS10	0.30	0.15	0.46	0.00	0.54

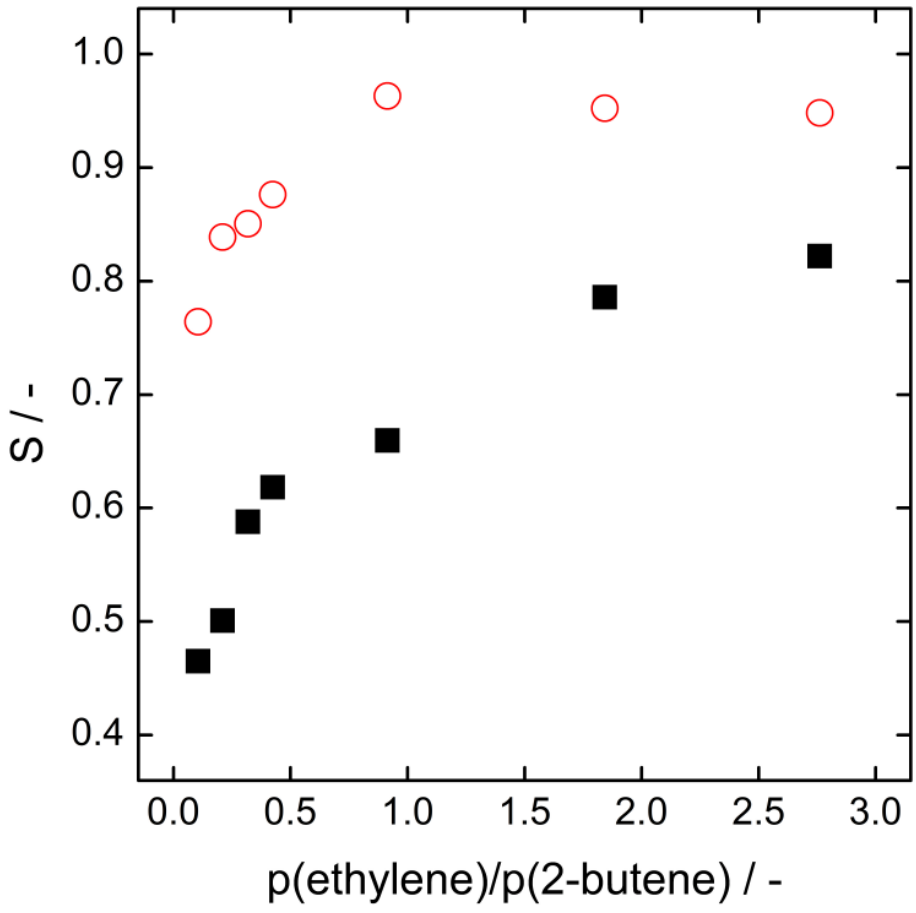

Figure ESI-1. Selectivity to propene (S) over (■) 0.15MoS70 and (○) 1.5MoS10 at different ratios of partial pressure (p) of ethylene to 2-butene at 423 K, 125 kPa total pressure and a conversion of 2-butene ranging between 0.13 and 0.44. The sum of the partial pressure of ethylene and *trans*-2-butene was kept between 0.96 and 1.14. Exact feed compositions are given in Table ESI-2.