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The effect of supported  $\text{MoO}_x$  structures on the reaction pathways of propene formation in the metathesis of ethylene and 2-butene

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# The effect of supported $\text{MoO}_x$ structures on the reaction pathways of propene formation in the metathesis of ethylene and 2-butene†

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The kind of surface  $\text{MoO}_x$  structures on  $\text{Al}_2\text{O}_3\text{-SiO}_2$  was found to determine propene selectivity in the metathesis of ethylene and 2-butene. Compared to isolated tetrahedral  $\text{MoO}_x$  species, their polymerized octahedral counterparts show significantly lower activity for isomerisation of 2- to 1-butene thus hindering non-selective metathesis of these butenes. In addition, they reveal higher ability to engage ethylene in propene formation.

Propene is a versatile building block in the chemical industry. Since the last twenty years its demand has continuously increased especially owing to the increasing production of polypropylene.<sup>1</sup> To accommodate the propene demand, the metathesis of ethylene and 2-butene to propene over a  $\text{WO}_x/\text{SiO}_2$  catalyst has been commercialized.<sup>2-4</sup> However, the selectivity of this process is hampered by the co-production of pentenes through metathesis of 1- and 2-butenes.<sup>5</sup> 1-Butene may either be introduced as part of the feed, which is typically derived from the  $\text{C}_4$ -cut of a steam cracker, or may be formed *via* 2- to 1-butene isomerisation over the metathesis catalyst. In order to achieve high propene selectivity, the metathesis reaction is industrially performed using a feed with an excess of ethylene.<sup>6</sup> From an economic viewpoint, operation using an ethylene-rich feed is not optimal, because of lower propene productivity than using a stoichiometric feed. To increase the productivity, it is essential to design catalysts producing propene as selective as possible. For this purpose, the origins governing propene selectivity must be comprehended.

To the best of the authors' knowledge, such studies have not been reported up to now, while activity-determining factors have been thoroughly investigated. For example, the rate of propene formation over Mo-containing catalysts, which are promising alternatives to  $\text{WO}_x/\text{SiO}_2$ , is influenced by (i) the support<sup>7,8</sup> and (ii) the structure of surface  $\text{MoO}_x$  species.<sup>9-11</sup> Recently, it has been demonstrated that Brønsted acidity of highly dispersed

tetrahedral and polymerized octahedral  $\text{MoO}_x$  species is also an essential activity-determining factor.<sup>8</sup>

Based on the above background, we disclose for the first time (i) the differences between supported tetrahedral and octahedral  $\text{MoO}_x$  species in their selectivity to propene in the metathesis of ethylene and 2-butene and (ii) the fundamental roots of these differences. Despite a similar intrinsic activity (Table S1 in ESI†), octahedral  $\text{MoO}_x$  species show propene selectivity above 90% compared to only 65% achieved over tetrahedral  $\text{MoO}_x$  species at similar ethylene conversion (10–12%) using a stoichiometric ethylene/*trans*-2-butene feed (Fig. 1). To explain these differences in selectivity, we investigated this reaction in a broad range of conversion of feed components with ethylene/*trans*-2-butene feeds varying in the ratio between 0 and 2.8 (Table S2 in the ESI†). Prefix *trans* is only used for feed compositions, while 2-butene stands for *cis*- and *trans*-2-butenes, because the former was not considered a reaction product. In addition, we systematically analysed possible molybdenum carbene species that may form from feed components and reaction products under consideration of a metallacyclobutane intermediate mechanism.<sup>12</sup>

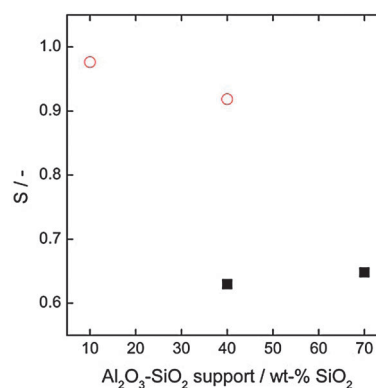


Fig. 1 Selectivity (S) to propene in the metathesis of ethylene and *trans*-2-butene over tetrahedral (■) and octahedral (○)  $\text{MoO}_x$  species on  $\text{Al}_2\text{O}_3\text{-SiO}_2$  supports with different content of  $\text{SiO}_2$ . Reaction conditions: 423 K, 125 kPa and ethylene/*trans*-2-butene/nitrogen = 5/5/1. Ethylene conversion was between 0.10 and 0.12.

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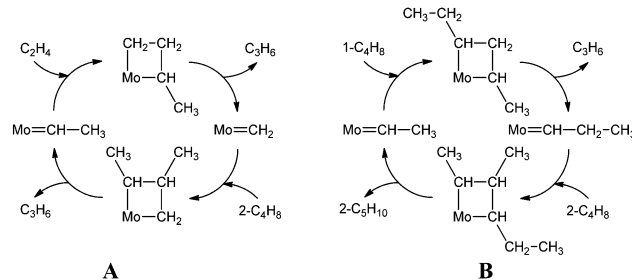
† Electronic supplementary information (ESI) available: Additional experimental section, tables and figure. See DOI: 10.1039/c4cc01827c



Catalysts were prepared by incipient wetness impregnation of  $\text{Al}_2\text{O}_3\text{-SiO}_2$  supports (Siral<sup>®</sup>, Sasol) with aqueous solutions of ammonium heptamolybdate (Riedel-de Haen). They are denoted  $\text{XMoSY}$ , where “X” stands for the nominal Mo loading ( $\text{Mo nm}^{-2}$ ) and “Y” for the  $\text{SiO}_2$  content (wt%) of the bare support. Supports and catalysts were characterized by  $\text{N}_2$  adsorption, ICP-OES, XRD, UV-vis and Raman spectroscopy,  $\text{H}_2$ -TPR and IR pyridine adsorption.<sup>8</sup> The obtained results revealed that all catalysts with  $0.15 \text{ Mo nm}^{-2}$  possess highly dispersed tetrahedral  $\text{MoO}_x$  species, while those with  $1.5 \text{ Mo nm}^{-2}$  contain polymerized octahedral  $\text{MoO}_x$ . Catalytic tests were carried out in fixed-bed reactors at 423 K and 125 kPa. Further experimental details are given in ESI<sup>†</sup>

To derive mechanistic insights into the effect of catalyst on propene selectivity presented in Fig. 1, we analysed how the selectivity to the target and side products depends on the degree of 2-butene conversion measured at contact times between 0.03 and  $1.10 \text{ s g ml}^{-1}$ . Such tests were performed with a standard ethylene/*trans*-2-butene/nitrogen = 5/5/1 feed over 0.15MoS70 and 1.5MoS10 representing the catalysts with tetrahedral and octahedral  $\text{MoO}_x$  species, respectively. This selectivity-conversion analysis helps to elucidate if and how the target reaction is influenced by side reactions like 2- to 1-butene isomerisation, metathesis of these butenes or metathesis of ethylene and pentene.<sup>5,6,13,14</sup> The obtained results are summarized in Fig. 2.

One can clearly see that the propene selectivity over 1.5MoS10 is around 97% at 10% 2-butene conversion and does not practically change with increasing conversion. From a mechanistic viewpoint, this selectivity-conversion relationship implies that propene is directly formed from 2-butene through its metathesis with ethylene (Scheme 1, A). This reaction scheme is not valid for 0.15MoS70 as concluded from the fact that the selectivity to propene is strongly influenced by 2-butene conversion. It increases from 44 to 79% with a corresponding increase in the conversion from 16 to 47%, but is always below the values obtained over 1.5MoS10. Since the increase in propene selectivity is coupled with a simultaneous decrease in 1-butene selectivity, we conclude that metathesis of 1- and 2-butenes strongly contributes to propene formation over 0.15MoS70 (Scheme 1, B). 1-Butene is primarily formed *via*



Scheme 1 Catalytic cycles of the metathesis of (A) ethylene and 2-butene and (B) 1- and 2-butene according to Chauvin.<sup>12</sup>

2-butene isomerisation, while dimerization of ethylene to 1-butene can be excluded because the latter olefin was not observed in a separate test with an ethylene/nitrogen = 1/16 feed. 2- to 1-Butene isomerisation is significantly faster than metathesis of 1- and 2-butenes to propene as evidenced by the high selectivity to 1-butene at low conversion of 2-butene. The low selectivity to pentene (Fig. 2), which should be formed in similar amounts as propene through metathesis of 1- and 2-butenes, may be related, for example, to its metathesis with ethylene to propene and 1-butene.

As the surface of our catalysts is only partly covered by  $\text{MoO}_x$  species, we also tested the corresponding bare supports to check their activity and selectivity. Both supports did not show any activity for propene formation but catalysed 2- to 1-butene isomerisation with a similar activity (Table S3 in the ESI<sup>†</sup>). Importantly, 1-butene was not observed over 1.5MoS10 at low 2-butene conversion, while significant amounts were detected over 0.15MoS70. This implies that the isomerisation rate (formation of 1-butene) over the latter catalyst is higher than the rate of 1-butene conversion through metathesis with 2-butene as otherwise 1-butene would not be observed. To estimate the contribution of the bare support to the isomerisation activity of 0.15MoS70, we calculated the rate of 1-butene formation; it is approximately 3.5 times higher over the catalyst than over the bare support (Table S3 in the ESI<sup>†</sup>). Bearing in mind that 0.15MoS70 also consumed 1-butene *via* metathesis with 2-butene, the difference in the isomerisation activity between the catalyst and the bare support must be even higher. Thus, 2- to 1-butene isomerisation is predominantly and propene formation is exclusively catalysed by  $\text{MoO}_x$ . Consequently, the selectivity-conversion relationship presented in Fig. 2 is primarily determined by the kind of  $\text{MoO}_x$  and not by the support. Considering the mechanism of olefin metathesis *via* molybdacyclobutane intermediates,<sup>12</sup> the effect of the  $\text{MoO}_x$  structure (tetrahedral *vs.* octahedral) on propene selectivity can be governed by (i) the formation of the suitable molybdenum carbene species ( $\text{Mo=CHR}$ ), (ii) the chemisorption of olefins on  $\text{MoO}_x$  species leading to  $\text{Mo=CHR}$  and (iii) the rates of formation of molybdacyclobutane intermediates and their decomposition to gas-phase metathesis products.

To derive insights into the kind of  $\text{Mo=CHR}$  required for selective propene formation, we have systematically analysed the possible reaction pathways occurring in the metathesis of ethylene and 2-butene. Considering the mechanism of propene metathesis on isolated  $\text{MoO}_x$ ,<sup>15</sup> we put forward that different primarily  $\text{Mo=CHR}$  species are formed upon reaction of

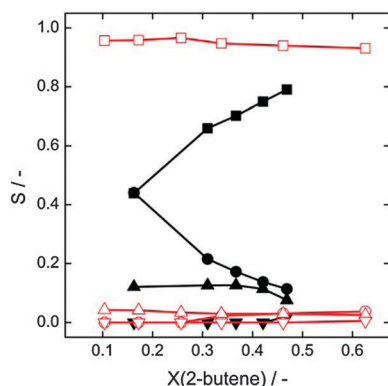
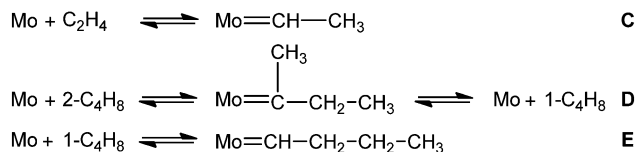


Fig. 2 Selectivity ( $S$ ) to propene (■, □), 1-butene (●, ○), pentene (▲, △) and hexene (▼, ▼) versus conversion ( $X$ ) of 2-butene over 0.15MoS70 (solid symbols) and 1.5MoS10 (open symbols). Reaction conditions: 423 K, 125 kPa and ethylene/*trans*-2-butene/nitrogen = 5/5/1.



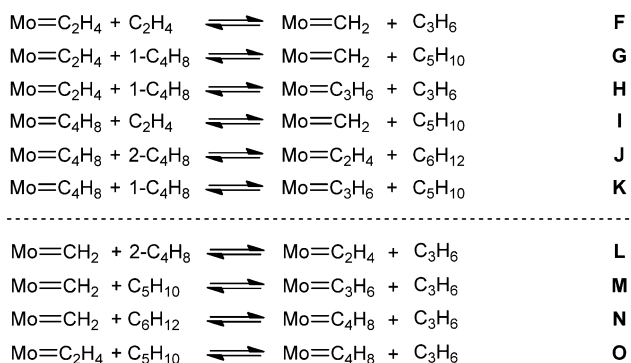


Scheme 2 Initial Mo=CHR generated by (C) ethylene, (D) 2-butene (including the isomerisation pathway of 2- to 1-butene) and (E) 1-butene.

ethylene and 2-butene with reduced MoO<sub>x</sub> (Mo) sites as shown in Scheme 2, C and D, respectively. This scheme additionally illustrates the formation of 1-butene *via* isomerisation (E) and its subsequent reaction with reduced Mo sites (F).

At low degrees of 2-butene conversion, *i.e.* low amounts of reaction products, feed olefins preferentially react with Mo=CHR formed from the feed components (pathways F–K in Scheme 3). Upon rising 2-butene conversion, secondary reactions involving reaction products and additionally formed Mo=CHR can result in propene (L–O in Scheme 3). Its formation is only possible when Mo=CH<sub>2</sub> and Mo=C<sub>2</sub>H<sub>4</sub> are involved in catalytic cycles (F, H and L–O in Scheme 3). Such metal carbene species are exclusively formed with participation of ethylene. Furthermore, a 100% selective propene production is only achieved if F is alternating with L (Scheme 1, A). Considering this knowledge and the observed propene formation over 0.15MoS70 and 1.5MoS10, both catalysts should possess Mo=CH<sub>2</sub> and Mo=C<sub>2</sub>H<sub>4</sub> species. Therefore, we can conclude that the MoO<sub>x</sub> structures have no principle influence on the ability to generate propene-forming carbene species. However, what are the fundamental origins for the different propene selectivity of 0.15MoS70 and 1.5MoS10 in Fig. 1 and 2?

To clarify the above question, we analysed the ability and activity of 0.15MoS70 and 1.5MoS10 (i) to generate propene *via* metathesis of 1- and 2-butenes (Scheme 1, B) and (ii) to catalyse 2- to 1-butene isomerisation. Catalytic tests with a *trans*-2-butene/1-butene/nitrogen (5/5/1) feed revealed that both catalysts produce propene with similar activity and selectivity (Table S4 in the ESI<sup>†</sup>). These rates are also close to those in the metathesis of ethylene and 2-butene. To indirectly check the isomerisation activity of 0.15MoS70 and 1.5MoS10, we carried out catalytic tests using a *trans*-2-butene/nitrogen (1/16) feed. Under this feed 2- to 1-butene



Scheme 3 (F–K) overall primary metathesis pathways and (L–O) secondary metathesis pathways only for propene formation. For simplification, we do not distinguish between isomeric structures of Mo=C<sub>4</sub>H<sub>8</sub> and isomers of pentene and hexene.

isomerization precedes metathesis of 1- and 2-butenes. Propene was formed over both catalysts, however, five times faster over 0.15MoS70 than over 1.5MoS10 (Table S5 in the ESI<sup>†</sup>). Moreover, at low 2-butene conversion, 1-butene was detected only over 0.15MoS70. Taking into account this information and similar intrinsic activity of both catalysts for 2- and 1-butenes metathesis (Table S4 in the ESI<sup>†</sup>), we can safely conclude that 0.15MoS70 shows significantly higher isomerisation activity than 1.5MoS10. This may be related to higher Brønsted acidity of the former catalyst.<sup>8</sup>

Another important difference between isolated tetrahedral and polymerized octahedral MoO<sub>x</sub> species is their ability to engage ethylene in propene formation. This conclusion was derived from analysing the reaction rates of propene formation ( $r_{\text{Mo}}(\text{propene})$ ) and ethylene consumption ( $r_{\text{Mo}}(\text{ethylene})$ ) in catalytic tests using reaction feeds with an ethylene/*trans*-2-butene ratio between 0.1 and 2.8. With increasing partial pressure of ethylene, a rising propene selectivity was observed (Fig. S1 in the ESI<sup>†</sup>). From a kinetic viewpoint,  $r_{\text{Mo}}(\text{propene})$  is a sum of rates of metathesis of 1- and 2-butenes and ethylene-assisted metathesis, while  $r_{\text{Mo}}(\text{ethylene})$  represents the latter process exclusively. Consequently, the ratio of  $r_{\text{Mo}}(\text{propene})/r_{\text{Mo}}(\text{ethylene})$  provides the contribution of metathesis of 1- and 2-butenes to overall propene formation. If this metathesis reaction did not run, the ratio of  $r_{\text{Mo}}(\text{propene})/r_{\text{Mo}}(\text{ethylene})$  would be equal to 2, which is typical for selective metathesis of ethylene and 2-butene to propene (Scheme 1, A). Fig. 3 illustrates this ratio as a function of partial pressures of ethylene and 2-butene. For 1.5MoS10, it decreases from 2.4 to 2.1 with an increase in the feed ratio of ethylene/*trans*-2-butene from 0.1 to 0.4 and remains constant upon further increasing partial pressure of ethylene. This means that propene is mainly produced through the metathesis of ethylene and 2-butene. This reaction is significantly faster than the metathesis of 1- and 2-butenes probably due to the low 2- to 1-butene isomerisation activity. Contrarily to 1.5MoS10, 0.15MoS70 containing isolated tetrahedral MoO<sub>x</sub> species generates propene faster from butenes than from ethylene and 2-butene. A value of  $r_{\text{Mo}}(\text{propene})/r_{\text{Mo}}(\text{ethylene})$  close to 2 was only achieved when using a feed with 2.8 times excess of ethylene over *trans*-2-butene. Moreover,  $r_{\text{Mo}}(\text{propene})/r_{\text{Mo}}(\text{ethylene})$  strongly increased with a decrease in ethylene partial pressure and reached 5.3 for the feed with an ethylene/*trans*-2-butene ratio of 0.1. These results evidence significantly lower activity (or lower concentration) of Mo=CHR species formed from tetrahedral MoO<sub>x</sub> species for converting ethylene compared to those originated from octahedral MoO<sub>x</sub>.

Based on the above discussion, we put forward that in addition to 2- to 1-butene isomerisation, the structure of MoO<sub>x</sub> influences (i) the rates of formation of Mo=CHR species from ethylene and butenes or their decomposition and (ii) the rates of reacting gas-phase olefins with Mo=CHR to produce molybdacyclobutane intermediates or to decompose them to other gas-phase olefins. The latter assumption is indirectly supported by previous DFT studies on the initial steps of ethylene interaction with Mo=CH<sub>2</sub> formed from monomeric and dimeric reduced MoO<sub>x</sub> supported on Al<sub>2</sub>O<sub>3</sub>.<sup>16</sup> The reactivity of individual sites was predicted to depend on their geometry and



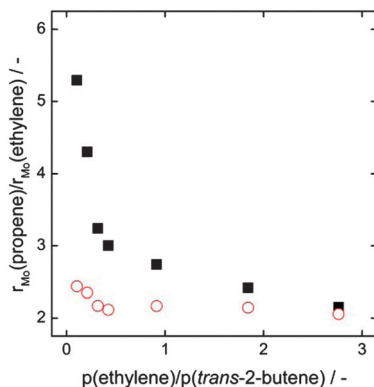


Fig. 3 Ratio of the propene formation rate related to the rate of ethylene consumption over (■) 0.15MoS70 and (○) 1.5MoS10 at different ratios of partial pressure ( $p$ ) of ethylene to *trans*-2-butene at 423 K, 125 kPa total pressure and a conversion of 2-butene ranging between 0.13 and 0.44. The sum of the partial pressure of ethylene and *trans*-2-butene was kept between 0.96 and 1.14.

electronic structure. For monomeric  $\text{MoO}_x$  sites, the formation of a stable molybdacyclobutane intermediate is kinetically favoured over the cycloreversal step into metathesis products, while the latter step is preferred on dimeric sites. These results might explain the low ability of 0.15MoS70 with isolated tetrahedral  $\text{MoO}_x$  to form propene with participation of ethylene. However, to draw a definitive conclusion about the reactivity of  $\text{Mo}=\text{CHR}$  formed from tetrahedral and octahedral  $\text{MoO}_x$  species, further deeper experimental and theoretical studies are required.

In summary, the results reported here demonstrate for the first time that the kind of supported  $\text{MoO}_x$  species is a key factor governing propene selectivity in the metathesis of ethylene and 2-butene. This is due to the fact that tetrahedral and octahedral  $\text{MoO}_x$  species accelerate different reaction pathways. 2- to 1-Butene isomerisation and metathesis of butenes over tetrahedral  $\text{MoO}_x$  species are faster than reactions

with participation of ethylene leading to propene. Compared to these species, metathesis of ethylene and 2-butene is significantly faster than other side reactions over octahedral  $\text{MoO}_x$  species. This is the reason for their high propene selectivity, which was even achieved under strong excess of 2-butene over ethylene. For deriving further fundamental details about the kinetics and the interaction of  $\text{Mo}=\text{CHR}$  with ethylene and 2-butene over differently structured  $\text{MoO}_x$  species, we are currently investigating these processes by means of *in situ* infrared spectroscopy and pulse experiments.

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