Stereoselectivity in the Metathesis Reaction of But-2-ene on a β-Titanium Oxide-supported Molybdenum Oxide

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Summary With $MoO_x/\beta\text{-}TiO_2$ as catalyst the stereoselective formation of *cis*- and *trans*-$[^2H_4]$but-2-ene is observed in the metathesis of equimolar mixtures of *cis*-$[^2H_0]$- and -$[^2H_8]$but-2-ene, and *trans*-$[^2H_0]$- and -$[^2H_8]$-but-2-ene, respectively, the yields of *cis*- and *trans*-but-2-ene from reactions of the corresponding pent-2-ene isomers are in good agreement, but metathesis of propene selectively yields *trans*-but-2-ene

METAL carbene and metallocyclobutane intermediates have been generally accepted for olefin metathesis reactions especially in homogeneous systems,[1] however, the process leading to initial formation of metal carbenes[2] and the *cis–trans* stereoselectivity in the olefins produced[3] still constitute interesting problems We now report the stereoselectivity observed in $[^2H_4]$but-2-ene ($CH_3CH{=}CDCD_3$) or $[^2H_0]$but-2-ene formation on a novel catalyst, $MoO_x/\beta\text{-}TiO_2$ ($2{\cdot}9 > x > 2{\cdot}3$),[4] on which the olefin metathesis reaction took place with neither intermolecular hydrogen scrambling nor isomerization through alkyl or carbonium ion intermediates [4,5] The reaction was carried out over 0·3 g of 6·7 wt% of $MoO_x/\beta\text{-}TiO_2$ catalyst in a closed circulation system of *ca* 350 ml volume

trans-But-2-ene consisting of $[^2H_0]$-, $[^2H_4]$-, and $[^2H_8]$-isomers and *cis*-$[^2H_4]$but-2-ene were formed in the reaction of a 1:1 mixture of *cis*-$[^2H_0]$- and *cis*-$[^2H_8]$-but-2-ene. The figure shows that only the $[^2H_0]$-, $[^2H_4]$-, and $[^2H_8]$-but-2-enes were formed in this reaction, and we conclude that the *trans*-but-2-ene is formed by the metathesis reaction on the $MoO_x/\beta\text{-}TiO_2$ catalyst [4,5] The $[^2H_4]$but-2-ene was composed of more than 60% of the *cis* form at the initial stage of the reaction, and the *cis/trans* ratio of the $[^2H_4]$but-2-ene decreased to reach an equilibrium value as the reaction proceeded In contrast, *trans*-$[^2H_4]$but-2-ene was produced with high selectivity in the early stages of

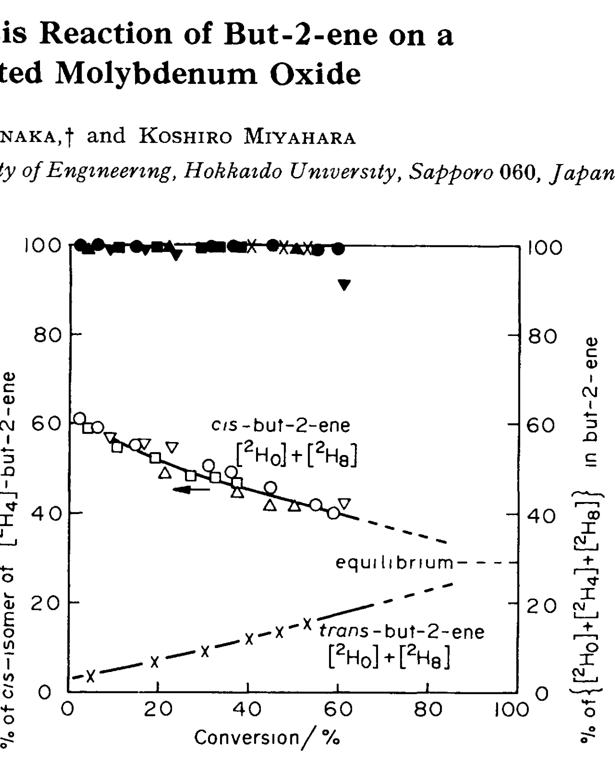

FIGURE Metathesis reaction of a 1:1 mixture of $[^2H_0]$- and $[^2H_8]$-but-2-ene on an $MoO_x/\beta\text{-}TiO_2$ catalyst ○, ● −10 °C, 32 2 mmHg total pressure, □, ■ −8 °C, 8 7 mmHg, △,▲ 25 °C, 4 5 mmHg, ▽, ▼ 25 °C, 37 5 mmHg, × 25 °C, 23 2 mmHg Open symbols, % of *cis*-isomer, filled symbols, % of $\{[^2H_0] + [^2H_4] + [^2H_8]\}$ Equilibrium conversion, 100%

the metathesis reaction of a 1:1 mixture of *trans*-[$^2H_0$]- and *trans*-[$^2H_8$]-but-2-ene. These results indicate that the *cis* or *trans* geometry of the starting material was largely retained in the [$^2H_4$]but-2-ene produced in the degenerate metathesis reaction of but-2-ene. This stereoselectivity is attributed to stability differences between the metallocyclobutane intermediates with various symmetries.[3d,f,g]

The productive metathesis reaction of pent-2-ene on this MoO_x/β-TiO_2 catalyst revealed the same degree of stereoselectivity in but-2-ene formation as that in the degenerate metathesis reaction of but-2-ene mentioned above. However, the *cis/trans* ratio was 0·2 for but-2-ene produced in the early stages of the metathesis reaction of propene on the present catalyst.

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