Super Active Catalysts, MoO_3/ and MoO_{3-x}/β-TiO_2 Activated with $SnMe_4$, for a Structure Retaining Alkene Metathesis

Katsumi Tanaka[a] **and Ken-ichi Tanaka***[b]

[a] *Research Institute for Catalysis, Hokkaido University Kita-ku, Sapporo 060, Japan*
[b] *The Institute for Solid State Physics, The University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106, Japan*

The activity for alkene metathesis on MoO_3/or MoO_{3-x}/β-TiO_2 ($0.1 < x < 0.7$) was enhanced more than 10^3 times after treating with $SnMe_4$, while the hydrogen scrambling as well as the double bond migration of the alkenes were not influenced by this treatment; the metathesis of inner alkenes on these activated catalysts was characteristic since the *cis* or *trans* conformation of starting molecules was retained in the metathesis products.

Metal carbene and metallacyclobutane are key intermediates in alkene metathesis, but the formation of carbenes from the alkene in the initiation process and the relative stability and/or the reactivity of the substituted metallacyclobutanes are still unsolved problems.[1]

We prepared highly active novel alkene metathesis catalysts by treating MoO_3/ or MoO_{3-x}/β-TiO_2 ($0.1 < x < 0.7$) with $SnMe_4$.[2] The MoO_3/ or MoO_{3-x}/β-TiO_2 (10—50 mg) was prepared, as described in the preceding paper,[3] in a closed circulation system (*ca.* 280 ml) then exposed to He (60 Torr) containing $SnMe_4$ vapour (1 Torr) at room temperature for 30 minutes and finally evacuated for 30 minutes at the same temperature. The treatment of the molybdenum oxide surfaces with $SnMe_4$ yielded a small amount of methane in the gas phase. This fact indicates the formation of some hydrogen deficient species on the surface, which may involve CH_2 species.[4] Alkene metathesis reactions on this $SnMe_4$ treated catalyst proceed catalytically, since the concentration of ^2H atoms in the alkenes was not diluted by the ^1H atoms from the preadsorbed $SnMe_4$, and the initial activity for metathesis was recovered by evacuation at 100 °C.

Table 1. Turnover frequencies (T.F.), *cis*/*trans* ratio of but-2-ene formed, and V_D/V_P ratio in the metathesis reaction of a 1 : 1 mixture of [$^2H_0$]- and [$^2H_6$]-propene.

Catalyst[a]	T.F.[b]	*cis*/*trans*-But-2-ene[c]	V_D/V_P
MoO_3/β-TiO_2	0	—	—
MoO_3/β-TiO_2 + $SnMe_4$	9.3×10^{-5}	>0.5	10
MoO_{3-x}/β-TiO_2	2.0×10^{-7}	<0.2	6.7
MoO_{3-x}/β-TiO_2 + $SnMe_4$	5.2×10^{-4}	<0.2	27

[a] Catalyst 0.5 g, pressure of C_3H_6 25 mmHg. [b] The rate of formation of ethylene (molecules per Mo atom s^{-1}). [c] Equilibrium value is 0.3.

Table 1 shows the results of the metathesis of a 1 : 1 mixture of [$^2H_0$]- and [$^2H_6$]-propene over various catalysts. By comparing the amount of [$^2H_2$]propene or [$^2H_4$]propene with the amount of ethylene ([$^2H_0$], [$^2H_2$], [$^2H_4$]) or but-2-ene ([$^2H_0$], [$^2H_4$], [$^2H_8$]), one can evaluate the relative contribution of the degenerate metathesis to the productive one, which is shown in the ratio V_D/V_P. The amount of CH_2 species remaining on the catalyst surface was estimated to correspond to less than 1% of the total number of Mo atoms. In spite of this, the turnover frequency (formation of C_2H_4 molecules per Mo atom s^{-1}) evaluated by assuming that all Mo atoms participate in the formation of C_2H_4 is about one tenth that of the most active catalyst which was prepared by adsorbing organomolybdenum complexes on Al_2O_3, Iwasawa *et al.*[5] Taking account of the fact that the ratio of V_D/V_P on MoO_{3-x}/β-TiO_2 increased about four times after treatment with $SnMe_4$, the activity of our catalyst might be comparable to that of the most active catalyst.

If a mixture of *cis*-$^2H_0$]- and *cis*-[$^2H_8$]-but-2-ene was contacted with the catalysts activated with $SnMe_4$, *trans*-[$^2H_4$]-, *cis*-[$^2H_0$]-, *cis*-[$^2H_4$]-, and *cis*-[$^2H_8$]-but-2-ene were formed

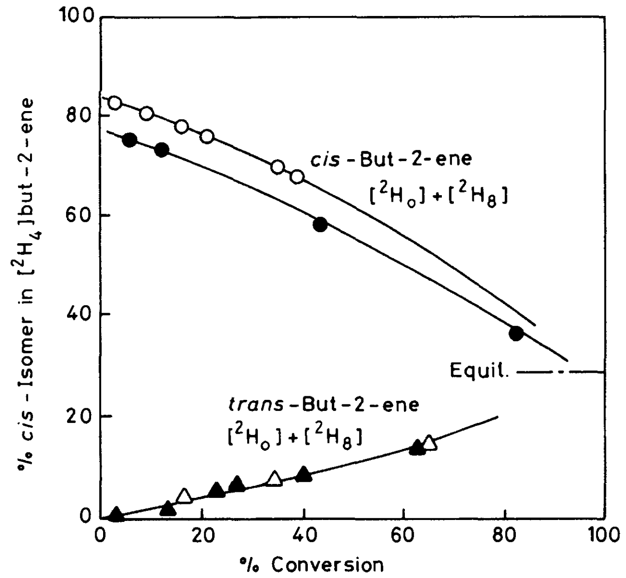

Figure 1. Metathesis reaction of a 1 : 1 mixture of [$^2H_0$]- and [$^2H_8$]-but-2-ene on SnMe$_4$ activated MoO$_3$/ and MoO$_{3-x}$/β-TiO$_2$ catalysts; ○, △ activated MoO$_{3-}$/β-TiO$_2$; ●, ▲ activated MoO$_{3-x}$/β-TiO$_2$; pressure of total but-2-ene, 16.0 mmHg; catalyst, 10—50 mg; reaction temperature, room temp.

Figure 1 shows the results of the reaction of an equimolar mixture of *cis*-[$^2H_0$]- and *cis*-[$^2H_8$]-but-2-ene on activated MoO$_3$/ and MoO$_{3-x}$/β-TiO$_2$: 85% *cis*-[$^2H_4$]but-2-ene was formed in the former case and 75% in the latter (in contrast, the metathesis over untreated MoO$_{3-x}$/β-TiO$_2$ gave *ca.* 60% selectivity in the structure retaining metathesis).[6] Hence, the activation with SnMe$_4$ increases not only the activity but also the structure retaining selectivity in the alkene metathesis reaction.

Figure 1 also shows the entirely selective (100%) formation of *trans*-[$^2H_4$]but-2-ene in the metathesis reaction of an equimolar mixture of *trans*-[$^2H_0$]- and *trans*-[$^2H_8$]-but-2-ene on the activated catalysts. The turnover frequency of *cis–trans* metathesis was about 10^{-3} on these catalysts, which is over 10^3 times more active than the non-treated catalysts.

Structure retaining selectivity such as *cis* giving *cis* and *trans* giving *trans* can be explained by the 1,3-interaction of methyls in metallacyclobutane, while stereoselectivity in the metathesis of α-olefins is attributable to the conformation of 2-substituted metallacyclobutane intermediates on non-activated MoO$_{3-x}$/β-TiO$_2$.[7]

In conclusion, the treatment of MoO$_3$/ or MoO$_{3-x}$/β-TiO$_2$ with SnMe$_4$ strictly controls the conformation of the 1,3-substituted metallacyclobutane, but has little influence on the conformation of the 2-substituted one.

Received, 27th February 1984; Com. 260

References

1 J. J. Rooney and A. Stewart, in 'Catalysis,' ed. C. Kemball, Specialist Periodical Reports, The Chemical Society, London, 1977, Vol. 1, p. 277; R. L. Banks, *ibid.*, 1981, Vol. 4, p. 100.

2 G. C. N. van den Aardweg, R. H. A. Bosma, and J. C. Mol, *J. Chem. Soc., Chem. Commun.*, 1983, 262.

3 Katsumi Tanaka, Ken-ichi Tanaka, and K. Miyahara, *J. Chem. Soc., Chem. Commun.*, 1979, 314.

4 E. L. Muetterties, *Inorg. Chem.*, 1975, **14**, 951.

5 Y. Iwasawa, H. Ichinose, S. Ogasawara, and M. Soma, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 1763.

6 Katsumi Tanaka, Ken-ichi Tanaka, and K. Miyahara, *J. Chem. Soc., Chem. Commun.*, 1980, 666.

7 Katsumi Tanaka, K. Miyahara, and Ken-ichi Tanaka, *J. Mol. Catal.*, 1982, **15**, 133.