CHEMISTRY LETTERS, pp. 171-172, 1989.

Propylene Metathesis by Use of Novel $TiCl_4$ or $Ti(O\text{-}i\text{-}Pr)_4$-treated Low Valent Lanthanide Particles (Sm and Yb)

Hayao IMAMURA,* Kazuyoshi KODA, Hiroshi MIURA, and Susumu TSUCHIYA
Department of Industrial Chemistry, Faculty of Engineering,
Yamaguchi University, 2557 Tokiwadai, Ube 755

$TiCl_4$ or $Ti(O\text{-}i\text{-}Pr)_4$-treated low valent, highly dispersed lanthanide particles (Sm and Yb) prepared by metal vapor deposition exhibited the activity for propylene metathesis at 333-473 K. Propylene was selectively converted to ethylene and but-2-ene.

Olefin metathesis is an interesting reaction, which was discovered in the early 1960s in the heterogeneous phase.[1] A large number of catalyst systems, mostly based on molybdenum, tungsten or rhenium have been reported to be active in metathesis.[2] We report on the novel use of low valent, highly dispersed lanthanide particles treated with $TiCl_4$ or $Ti(OCH(CH_3)_2)_4$ ($Ti(O\text{-}i\text{-}Pr)_4$) for this reaction.

The low valent and highly dispersed lanthanide particles[3] were prepared by vaporizing the Sm or Yb metal atoms into a frozen tetrahydrofuran (THF) matrix (referred to as Sm/THF and Yb/THF). BET measurements yielded surface area estimates for Sm/THF and Yb/THF obtained in this way as 50-70 and 30-40 m^2/g, respectively. The treatment with Ti-compounds was conducted by adding a solution of $TiCl_4$ or $Ti(O\text{-}i\text{-}Pr)_4$ in methylcyclohexane or tetrahydrofuran to the

Table 1. Results of propylene metathesis by lanthanide-Ti compound[3]

Catalyst[b]		Activation	Metathesis activity
Lanthanide	Ti-compound/mmol	temperature[c]/K	mmol $min^{-1}g^{-1}$
Sm/THF	-	473	-[d]
Sm/THF	$TiCl_4$/0.26	473	9.0×10^{-5}[d]
Sm/THF	$TiCl_4$/0.52	373	4.5×10^{-4}[d]
Sm/THF	$TiCl_4$/0.52	523	2.9×10^{-3}[d]
Sm/THF	$TiCl_4$/0.58	473	5.3×10^{-4}[d]
Sm/THF	$Ti(O\text{-}i\text{-}Pr)_4$/0.49	298	2.4×10^{-3}[e]
Yb/THF	-	473	-[e]
Yb/THF	$Ti(O\text{-}i\text{-}Pr)_4$/0.33	298	7.0×10^{-4}[e]

a) The reaction was conducted by admitting propylene (90 Torr). b) The catalyst system is represented by the amount of Ti compound addition to the lanthanide powder (1 g). c) Evacuation treatment for 2 h. d) Initial activity at 373 K. e) Initial activity at 473 K.

lanthanide powders, respectively. The mixture was stirred at room temperature and then was dried under vacuum. The catalytic activity was tested in a standard recirculation system.

On addition of the Ti-compounds to low valent, highly dispersed lanthanide particles (Sm/THF and Yb/THF), conversion into active catalysts for olefin disproportionation occurred. Judging from the products obtained, olefin metathesis reaction occurred certainly; thus using propylene as a reactant, ethylene and butene were effectively produced, and vice versa, the mixture of ethylene and but-2-ene was converted to propylene. Table 1 shows some of the results obtained and a typical metathesis reaction of propylene in the presence of Sm-$TiCl_4$ is shown in Fig. 1. The reaction proceeded selectively to form ethylene and but-2-ene. The conversion of propylene was increased with an increase in pressure of propylene in the range of 30 to 100 Torr. But-2-ene pridominated, whereas the yield of but-1-ene was usually slight. The trans : cis ratio in the but-2-ene was relatively high (3-5). The composition of butenes varied slightly during the reaction, but the type of butene composition obtained was different from that upon isomerization. The Yb-Ti compound systems similarly catalysed the conversion of propylene at 473 K.

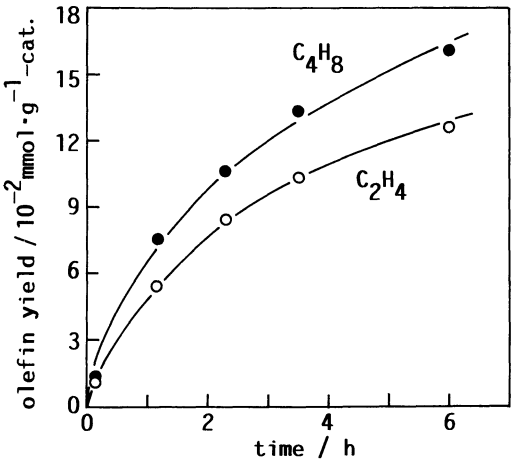

Fig. 1. The reaction of propylene (87 Torr) over Sm-$TiCl_4$ at 373 K.

The dependence of $TiCl_4$ and Ti(O-*i*-Pr)$_4$ addition on the metathesis activity was observed. For example, for the Sm-$TiCl_4$ system the activity increased with $TiCl_4$ addition and reached a maximum around 0.52-0.58 mmol of $TiCl_4$ added to Sm/THF (1 g) (Table 1). This indicates that the suitable catalysts are those in which the amounts of $TiCl_4$ added are roughly comparable to the values of the surface samarium species estimated from the surface area. Ti(O-*i*-Pr)$_4$ exhibited a simmilar manner for Sm/THF and Yb/THF. Further, through an investigation of catalyst treatment variables such as activation temperature this variable exerted a pronounced effect on the catalytic activity. The metathesis activity of the $TiCl_4$-treated lanthanide catalysts appeared upon evacuation treatment at ca. 473 K or above, whereas the Sm (or Yb)-Ti(O-*i*-Pr)$_4$ system exhibited higher activity when evacuated at 373 K or below. Although the metathesis catalysts containing Ti-compounds are known,[2] such combinations of lanthanides with Ti-compounds constitute a novel catalyst system. Detailed studies of the catalyst nature and mechanistic considerations are continuing in our laboratory.

References
1) R. L. Banks and G. C. Bailey, Ind. Eng. Chem. Prod. Res. Dev., 3, 170 (1964); R. L. Banks, Top. Curr. Chem., 25, 39 (1972). 2) J. C. Mol and J. A. Moulijn, "Catalysis, Science and Technology," ed by J. R. Anderson and M. Boudart, Springer-Verlag Berlin (1987), Vol. 8, Chap. 2, p. 69. and references therein. 3) H. Imamura, A. Ohmura, and S. Tsuchiya, J. Catal., 96, 139 (1985); H. Imamura, E. Haku, and S. Tsuchiya, Lanthanide Actinide Res., 2, 79 (1987); H. Imamura, K. Kitajima, and S. Tsuchiya, Chem. Lett., 1988, 249.

(Received November 10, 1988)