

## Novel Catalyst, $\text{MoO}_x\text{-}\beta\text{-TiO}_2$ , for the Olefin Metathesis Reaction with No Hydrogen Scrambling

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**Summary** A novel catalyst is reported on which the metathesis reaction of olefins proceeds without hydrogen scrambling or isomerization through alkyl or carbonium ion intermediates: the catalyst was prepared by treating reduced  $\text{MoO}_x\text{-}\beta\text{-TiO}_2$  with a mixture of  $\text{N}_2\text{O}$  and  $\text{H}_2$  at 200 °C.

A VARIETY of mechanisms and/or intermediates have been proposed for the olefin metathesis reaction.<sup>1</sup> Recent developments suggest that metal-carbene complexes are intermediates,<sup>2</sup> and the way in which the relative reactivities of these complexes depend on the M-C bond length is now one of the most interesting problems in rationalising the selectivity of this reaction. A difficult problem encountered with in homogeneous or heterogeneous catalysts is the simultaneous hydrogen scrambling and isomerization of olefins during the metathesis reaction. In general, the isomerization taking place simultaneously with the metathesis reaction can be suppressed by adding basic substances.<sup>3</sup> We here report a novel metathesis catalyst on which neither hydrogen scrambling nor isomerization occur during the metathesis reaction.

This catalyst was prepared by impregnating ammonium molybdate on to amorphous  $\beta\text{-TiO}_2$ , which was made from  $\beta$ -titanic acid ( $\text{H}_2\text{TiO}_3$ ) by boiling precipitated titanium

hydroxide for several hours. When this catalyst was reduced with hydrogen or carbon monoxide at 500 °C for 1 h, three distinct e.s.r. peaks, arising from  $\text{Mo}^{5+}$  ions in different environments, were observed at liquid nitrogen temperature; one of these peaks broadened and collapsed at room temperature.<sup>4</sup> These three molybdenum ions behave differently in various catalytic reactions.<sup>5</sup> Monitoring the surface by e.s.r. spectroscopy showed that if the reduced catalyst was treated with a mixture of  $\text{N}_2\text{O}$  and  $\text{H}_2$  at 200 °C, the surface underwent partial reoxidation where a steady reaction of  $\text{N}_2\text{O}$  and  $\text{H}_2$  occurred. This partially reoxidized surface showed unique properties in the olefin metathesis reaction. The role that the reoxidation with  $\text{N}_2\text{O}$  and  $\text{H}_2$  plays is not clear at present, and the effect of the water formed during the treatment needs to be examined. Table 1 shows the results for a catalyst which had been treated with a mixture of  $\text{N}_2\text{O}$  (180 Torr) and  $\text{H}_2$  (209 Torr) at 200 °C for 60 min and then evacuated at 500 °C for 2 h. The reaction was performed in a closed circulation system (347 ml), and the turn-over number was estimated to be *ca.*  $10^{-3}$  molecules  $\text{Mo}^{-1}\text{min}^{-1}$  providing that all the molybdenum ions are effective for the reaction; however, the reaction may proceed on a limited number of sites. It is obvious that *cis-trans* isomerization is brought about entirely by the metathesis reaction, and little hydrogen

TABLE 1. Reaction of a mixture of *cis*-[ $^2\text{H}_0$ ]but-2-ene and *cis*-[ $^2\text{H}_8$ ]but-2-ene (total pressure 56.2 Torr) over 0.3 g of catalyst at room temperature.

Product	Time/min	% Composition	% Deuterium distribution								
			$^2\text{H}_0$	$^2\text{H}_1$	$^2\text{H}_2$	$^2\text{H}_3$	$^2\text{H}_4$	$^2\text{H}_5$	$^2\text{H}_6$	$^2\text{H}_7$	$^2\text{H}_8$
<i>cis</i> -But-2-ene	0	100.0	48.4	0	0	0	0	0	0	4.0	47.6
	300	82.3	44.2	0	0	0.9	9.5	0	0	3.5	41.9
	960 <sup>a</sup>	49.1	30.2	0.8	0.2	3.4	27.6	0.6	0.6	3.1	33.9
<i>trans</i> -But-2-ene	0	0	—	—	—	—	—	—	—	—	—
	300	17.0	2.2	1.4	0.1	1.8	37.9	0	0	3.0	27.6
	960 <sup>a</sup>	47.1	25.0	3.9	0.3	2.7	39.0	2.0	0.3	3.5	22.9

<sup>a</sup> After 960 min 0.7% of but-1-ene, 2.6% of propene, and 0.6% of pentene were obtained.

TABLE 2. Reaction of a mixture of [ $^2\text{H}_0$ ]propene and [ $^2\text{H}_6$ ]propene (total pressure 44.0 Torr) over 1.0 g of catalyst at room temperature.

Product	Time/min	% Com- position	% Deuterium distribution								
			$^2\text{H}_0$	$^2\text{H}_1$	$^2\text{H}_2$	$^2\text{H}_3$	$^2\text{H}_4$	$^2\text{H}_5$	$^2\text{H}_6$	$^2\text{H}_7$	$^2\text{H}_8$
Propene	0	100.0	53.8	0	0	0	0	1.4	44.8	—	—
	310	90.2	32.5	1.5	21.0	1.5	19.5	1.9	22.1	—	—
Ethylene	0	0	—	—	—	—	—	—	—	—	—
	310	7.4	30.2	5.5	45.3	2.9	16.1	—	—	—	—
<i>trans</i> -But-2-ene	0	0	—	—	—	—	—	—	—	—	—
	310	1.9	31.5	1.1	0.4	2.5	46.4	0.7	0.4	1.4	15.7
<i>cis</i> -But-2-ene	0	0	—	—	—	—	—	—	—	—	—
	310	0.5	30.7	1.2	1.0	2.5	43.7	1.1	0.5	2.0	17.1

scrambling takes place simultaneously. The reaction of [ $^2\text{H}_0$ ]- and [ $^2\text{H}_6$ ]-propene at room temperature is summarized in Table 2, where the catalyst had been pretreated with a mixture of  $\text{N}_2\text{O}$  (105 Torr) and  $\text{H}_2$  (102 Torr) at 200 °C for 70 min before evacuation at 500 °C for 3 h. It is clear that the formation of [ $^2\text{H}_2$ ]- + [ $^2\text{H}_4$ ]-propene is far more rapid than that of ethylene and but-2-ene, and a rough estimation indicates that degenerate metathesis is about ten-fold faster than non-degenerate metathesis giving ethylene. The reaction between [ $^2\text{H}_0$ ]- and [ $^2\text{H}_6$ ]-but-1-ene gave similar results on this catalyst, *i.e.*, degenerate metathesis was about fourteen-fold faster than non-degenerate meta-

thesis. It is clear from Table 2 that the methylene group in propene exchanges rapidly by the degenerate metathesis reaction but intermolecular hydrogen exchange does not proceed appreciably; similar results were obtained for but-1-ene. N.m.r. spectroscopic analysis of the propene formed in the reaction of [ $^2\text{H}_4$ ]-ethylene and [ $^2\text{H}_0$ ]-but-2-ene showed no methylenic hydrogen, which indicates almost complete metathesis with no accompanying isomerization or hydrogen scrambling.

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