

## Selective Promotion of the Catalytic Ethene Homologation Reaction by KOH on an MoO<sub>x</sub>/SiO<sub>2</sub> Catalyst

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Ethene homologation activity on a reduced MoO<sub>x</sub>/SiO<sub>2</sub> catalyst was enhanced more than 10 times by a modification of the catalyst with KOH, while activity and selectivity in alkene metathesis were unaffected.

Since the discovery of the unique reaction of ethene to form propene by Rooney *et al.*,<sup>1</sup> homologation reactions of alkenes<sup>2</sup> and alkanes<sup>3</sup> have attracted much interest because these reactions are presumed to occur *via* metal carbene and metallacyclobutane intermediates which are the most plausible species for alkene metathesis reactions.<sup>4</sup> In this paper, we report that addition of potassium to an MoO<sub>x</sub>/SiO<sub>2</sub> catalyst greatly enhanced ethene homologation reaction activity without any change in alkene metathesis activity or hyperfine selectivities.

Kiesel gel 60 silica was immersed in an aqueous solution of ammonium molybdate and dried in air at 120 °C overnight to obtain a loading of 2.8 mol % MoO<sub>3</sub>/SiO<sub>2</sub>. KOH-doped silica (from aqueous KOH, calcined in air at 600 °C for 6 h) was used to prepare MoO<sub>3</sub>/K-SiO<sub>2</sub> (containing 2.8 mol % of MoO<sub>3</sub> and 0.28 mol % of K), by heating slowly from room temperature to 500 °C *in vacuo*. Catalysts A, B, and C were then obtained as follows. Catalyst A was MoO<sub>x</sub>/SiO<sub>2</sub> treated with H<sub>2</sub> at 500 °C for 1 h. Catalyst B was MoO<sub>x</sub>/SiO<sub>2</sub> obtained by the reoxidation of catalyst A with a 1 : 1 mixture of N<sub>2</sub>O and H<sub>2</sub> at 200 °C for 1 h. Catalyst C was MoO<sub>x</sub>/K-SiO<sub>2</sub> reduced with H<sub>2</sub> at 500 °C for 1 h. The catalysts were finally evacuated at 500 °C for 1 h. The catalyst treatment and the reactions were carried out in a closed glass circulation system with a volume of 260 ml.

When a mixture of [<sup>12</sup>C<sub>2</sub>]- and [<sup>13</sup>C<sub>2</sub>]-ethene was contacted with the catalysts A–C, the metathesis reaction giving [<sup>13</sup>C<sub>1</sub>]-ethene and the homologation reaction forming propene were found to occur (Figure 1). An induction period was observed for the homologation reaction, but not for the

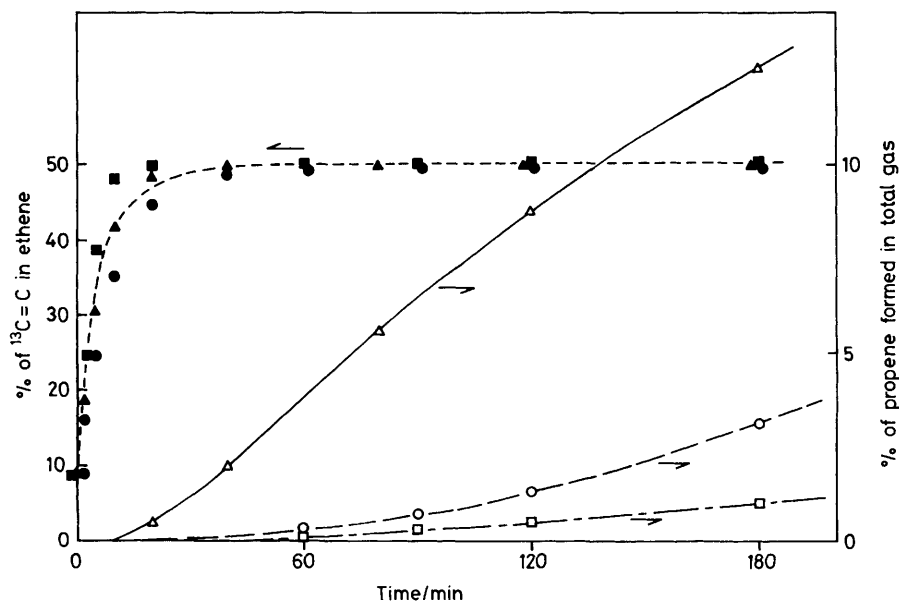
metathesis reaction. It is noteworthy that the ethene homologation reaction was considerably increased by an addition of potassium (catalyst C), but the metathesis reaction was not influenced at all. After 180 min of the reaction with ethene containing 9.1% [<sup>13</sup>C<sub>1</sub>]- and 42.3% [<sup>13</sup>C<sub>2</sub>]-ethene on catalyst C, propene comprised 12.5% of the total gas, with isotopic distribution [<sup>13</sup>C<sub>0</sub>], 17.9%; [<sup>13</sup>C<sub>1</sub>], 40.3%; [<sup>13</sup>C<sub>2</sub>], 32.7%; and [<sup>13</sup>C<sub>3</sub>], 9.1%. If propene is formed by the reaction of either <sup>12</sup>CH<sub>2</sub> or <sup>13</sup>CH<sub>2</sub> with ethene, approximately equal amounts of <sup>13</sup>C-isotopomers of propene would be formed provided there is no isotope effect. This was not the case, and intramolecular hydrogen shift reactions as well as degenerate metathesis of the propene are presumed to be responsible for the <sup>13</sup>C distribution obtained.

Table 1 shows the results of the metathesis reaction of a 1 : 1 mixture of [<sup>12</sup>C<sub>3</sub>]- and [<sup>13</sup>C<sub>3</sub>]-propene on catalysts A and C. Turnover frequency was evaluated by assuming that all Mo atoms participate in the formation of ethene. One can evaluate the relative contributions of degenerate and produc-

**Table 1.** Turnover frequencies (T.F.), *cis/trans* ratios of but-2-ene formed, and V<sub>D</sub>/V<sub>P</sub> ratios (see text) in the metathesis reaction of a 1 : 1 mixture of [<sup>12</sup>C<sub>3</sub>]- and [<sup>13</sup>C<sub>3</sub>]-propene at room temperature.

Catalyst <sup>a</sup>	T.F. <sup>b</sup>	<i>cis/trans</i> <sup>c</sup>	V <sub>D</sub> /V <sub>P</sub>
A	4.5 × 10 <sup>-4</sup>	0.5	7.6
C	5.0 × 10 <sup>-4</sup>	0.5	8.1

<sup>a</sup> Catalyst, 20 mg; total pressure 6.9 mmHg. <sup>b</sup> Rate of formation of ethene (molecules per Mo atom s<sup>-1</sup>). <sup>c</sup> Equilibrium value is 0.3.



**Figure 1.** The reaction of a 1 : 1 mixture of [<sup>12</sup>C<sub>2</sub>]- and [<sup>13</sup>C<sub>2</sub>]-ethene at room temperature. ●: catalyst, A, 0.5 g; total ethene, 10.2 mmHg, □: catalyst B, 0.5 g; 14.5 mmHg, △: catalyst C, 0.5 g; 14.6 mmHg.

tive metathesis ( $V_D/V_P$ ) by comparing the amount of [ $^{13}\text{C}_1$ ]- and [ $^{13}\text{C}_2$ ]-propene with the amount of ethene and but-2-ene. Since  $V_D/V_P$  ratios are almost equal on catalysts A (7.6) and C (8.1), and the turnover frequencies on these two catalysts are similar, we concluded that potassium has no effect on the alkene metathesis reaction.

In conclusion, addition of potassium to  $\text{MoO}_x/\text{SiO}_2$  has a marked influence on alkene homologation reactions but no effect on metathesis reactions, an important finding with respect to reactivity and selectivity.

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