

## Mixed-oxide Catalysts for the Metathesis of Functionalized Alkenes

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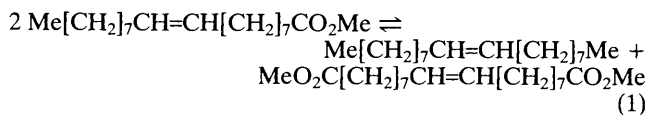
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Low-rhenium-loading  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3\text{-MR}_4$  (M = Sn or Pb; R = Me, Et, or Bu) catalysts show good activity at room temperature ( $293 \pm 2$  K) for the metathesis of functionalized alkenes, such as unsaturated esters, when they are modified with  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$ , or  $\text{WO}_3$ .

To date the system  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3\text{-SnR}_4$  (R = Me, Et, or Bu) is the most active catalyst for the heterogeneous metathesis of alkenes bearing certain functional groups, such as unsaturated esters, nitriles, *etc.*<sup>1-3</sup> Although this catalyst system has many advantages over its homogeneous counterparts, catalysts with a low rhenium content show negligible activity for meta-

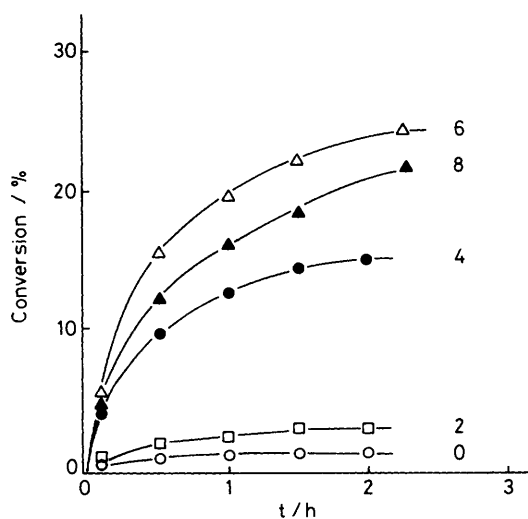
thesis.<sup>4,5</sup> Moreover, the activity for the metathesis of functionalized alkenes of catalysts with a higher rhenium content is still too low for practical applications of this potentially highly useful reaction. Therefore, also considering the high cost of rhenium compounds, it is important to develop catalysts which are more active for the metathesis of functionalized alkenes.

Here we report the preparation and activities of  $V_2O_5$ ,  $WO_3$ , or  $MoO_3$ -modified low-rhenium-loading catalysts for the metathesis of methyl oleate (*Z*-methyl octadec-9-enoate), a well known representative of unsaturated carboxylic esters (equation 1). The catalysts were prepared by impregnation of



$\gamma$ -alumina (Ketjen, CK 300,  $195 \text{ m}^2 \text{ g}^{-1}$ ,  $185\text{--}250 \mu\text{m}$ ) with such an amount of an aqueous solution of  $\text{NH}_4\text{ReO}_4$  as to obtain a 3 wt%  $\text{Re}_2\text{O}_7$  on  $\text{Al}_2\text{O}_3$  catalyst, followed by impregnation with an aqueous solution of  $(\text{NH}_4)_2\text{WO}_4$ ,  $\text{NH}_4\text{VO}_3$ , or  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , respectively. After each impregnation, the catalysts were dried at 383 K. They were calcined, activated, and used for the reaction as described earlier.<sup>2</sup> The atomic ratios and the weight percentages reported are nominal, calculated from the amount of the corresponding salts used for the impregnation. The reactions were carried out in stirred glass batch reactors under argon at room temperature ( $293 \pm 2 \text{ K}$ ). In a typical example, 100 mg of catalyst, 1 ml of a solution of  $\text{SnMe}_4$  ( $7.2 \mu\text{mol}$ ) in hexane, and  $250 \mu\text{l}$  ( $7.37 \text{ mmol}$ ) of methyl oleate were introduced in that order. The reaction was followed by g.c. and conversions were calculated as  $(2 \times \text{alkene}) / (2 \times \text{alkene} + \text{monoester})$  in the liquid phase.

Figure 1 shows the conversion as a function of the reaction time for the  $\text{MoO}_3 \cdot \text{Re}_2\text{O}_7 / \text{Al}_2\text{O}_3$  catalysts with varying Mo:Re atomic ratios (Re:Al atomic ratio kept at 1:154), using  $\text{SnMe}_4$  as co-catalyst. It appears that the ternary catalyst systems are much more active than the binary system  $\text{Re}_2\text{O}_7 / \text{Al}_2\text{O}_3$ . Similar results were obtained with the corresponding tungsten- and vanadium-containing catalysts. Although  $\text{MoO}_3$  and  $\text{WO}_3$  on alumina themselves are well known metathesis catalysts, they are not active at room temperature.  $V_2O_5$  on alumina is not a metathesis catalyst at all. Even when promoted with  $\text{SnR}_4$  these catalysts are not active for the metathesis of functionalized alkenes. It is,



**Figure 1.** Conversion of methyl oleate using  $\text{MoO}_3 \cdot \text{Re}_2\text{O}_7 / \text{Al}_2\text{O}_3$ - $\text{SnMe}_4$  catalysts as a function of the reaction time; the numbers after the curves are Mo:Re atomic ratios.

therefore, likely that in our case at least one rhenium atom per active centre is necessary for the catalytic activity.

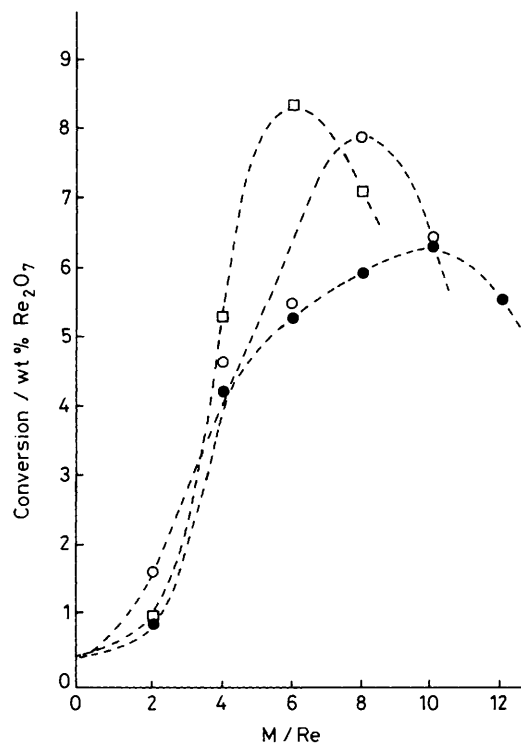
Figure 2 shows the promoting effect of adding the third metal oxide to the binary catalyst as a function of varying the M:Re atomic ratios (where M = Mo, V, or W). The catalytic activity is expressed as the conversion per wt%  $\text{Re}_2\text{O}_7$ . The results show that for each ternary system an optimal M:Re ratio exists. This ratio depends on the third metal oxide. That this optimal ratio is rather high suggests that multi-atomic species or metal-oxide clusters are responsible for generating active structures for the reaction. Since catalysts prepared by co-impregnation or by stepwise impregnation in the reverse order showed lower activity, a scavenger-like function<sup>6</sup> or prevention of a possible loss of  $\text{Re}_2\text{O}_7$  during the activation due to the outside metal oxide layer may be envisaged.

The oxides used here are already known to have a promoting effect on  $\text{Re}_2\text{O}_7 / \text{Al}_2\text{O}_3$  catalysts for the metathesis of simple alkenes.<sup>7</sup> However, they have not been used in combination with  $\text{SnR}_4$  for the metathesis of functionalized alkenes.

Other co-catalysts of the type  $\text{SnR}_4$  (*e.g.* R = Et or Bu) or  $\text{PbR}_4$  (R = Et or Bu) can be used too.  $\text{SnEt}_4$  and  $\text{SnBu}_4$  give an even higher activity than  $\text{SnMe}_4$  does, while  $\text{PbEt}_4$  and  $\text{PbBu}_4$  give an activity comparable to  $\text{SnMe}_4$ .

Preliminary results show that these ternary catalyst systems are also active for the metathesis of other functionalized alkenes, *e.g.* other unsaturated esters, unsaturated nitriles, *etc.*

The ternary catalysts have all the advantages of the  $\text{Re}_2\text{O}_7 / \text{Al}_2\text{O}_3$ - $\text{SnR}_4$  system, *e.g.* mild reaction conditions,



**Figure 2.** Conversion/wt%  $\text{Re}_2\text{O}_7$  for the metathesis of methyl oleate in the presence of ternary oxide catalysts, based on 3 wt%  $\text{Re}_2\text{O}_7$  on  $\text{Al}_2\text{O}_3$  as a function of their M:Re (M = Mo, W, or V) atomic ratio, after 90 min reaction time.  $\square$   $\text{MoO}_3 \cdot \text{Re}_2\text{O}_7 / \text{Al}_2\text{O}_3$ - $\text{SnMe}_4$  system;  $\circ$   $\text{WO}_3 \cdot \text{Re}_2\text{O}_7 / \text{Al}_2\text{O}_3$ - $\text{SnMe}_4$  system;  $\bullet$   $\text{V}_2\text{O}_5 \cdot \text{Re}_2\text{O}_7 / \text{Al}_2\text{O}_3$ - $\text{SnMe}_4$  system.

high selectivity, and re-usability, while the price of the catalysts is lower than the  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3\text{-SnR}_4$  catalyst for obtaining the same conversion.

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