$Re_2O_7/SiO_2{\cdot}Al_2O_3$–$SnR_4$ or –PbR_4, a Highly Active Catalyst for the Metathesis of Functionalized Alkenes

Xu Xiaoding* and J. C. Mol

University of Amsterdam, Institute of Chemical Technology, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Low-rhenium-loading $Re_2O_7/SiO_2{\cdot}Al_2O_3$–$SnR_4$ or –PbR_4 (R = alkyl) catalysts show high activity for the metathesis of functionalized alkenes at 293 ± 2 K, which is attributed to their high Brönsted acidity.

Alkene metathesis has many potential synthetic and industrial applications.[1,2] It provides an alternative way of preparing useful materials *via* a one-step reaction and can also be used for structural analysis of compounds that contain unsaturated bonds. Metathesis of functionalized alkenes is especially attractive for synthesis of distinct compounds which are difficult to obtain *via* other methods.[3—5] Re_2O_7/Al_2O_3–SnR_4 was the first system described as an active heterogeneous catalyst for the metathesis of functionalized alkenes; catalysts with 10—20 wt% Re_2O_7 are active and highly selective at room temperature.[6,7] However, the price of rhenium compounds is high and catalysts with low rhenium loadings have only negligible activity.[7] Recently, we reported that modification of these catalysts with MoO_3, V_2O_5, or WO_3 gives better results.[8]

We now report a new series of low-rhenium loading catalysts, *i.e.* $Re_2O_7/SiO_2{\cdot}Al_2O_3$–$MR_4$ (M = Sn or Pb, R = Me, Et, or Bu) that show an even higher activity than the catalysts known so far.

Three types of 250—500 µm Ketjen $SiO_2{\cdot}Al_2O_3$ supports were used: HA, 374 $m^2\,g^{-1}$, 24.3 wt% Al_2O_3; LAL, 144 $m^2\,g^{-1}$, 15.3 wt% Al_2O_3; and LAH, 460 $m^2\,g^{-1}$, 13.0 wt% Al_2O_3. These supports were impregnated with an aqueous solution of ammonium per-rhenate, followed by drying at 383 K. For comparative experiments Re_2O_7/Al_2O_3 catalysts were prepared in the same way, but impregnated on γ-alumina (Ketjen, CK 300, 185—250 µm, 195 $m^2\,g^{-1}$). The catalysts were activated as described earlier.[6] The weight percentages of rhenia in the different catalysts were calculated from the amount of ammonium per-rhenate used for the impregnation. Methyl oleate (*Z*-methyl octadec-9-enoate) (equation 1), a typical functionalized alkene, was used as a substrate and $SnEt_4$ (Aldrich Europe) was used as a co-catalyst, unless otherwise mentioned. The equilibrium conversion for this reaction is about 50%.

$$2\,Me[CH_2]_7CH{=}CH[CH_2]_7CO_2Me \rightleftharpoons Me[CH_2]_7CH{=}CH[CH_2]_7Me + MeO_2C[CH_2]_7CH{=}CH[CH_2]_7CO_2Me \quad (1)$$

Metathesis experiments were carried out as described earlier,[8] at room temperature (293 ± 2 K). In a typical reaction 100 mg of catalyst, 1 ml of a solution of $SnEt_4$ in hexane (7.2 µmol), and 250 µl (737 µmol) of methyl oleate were introduced in that order.

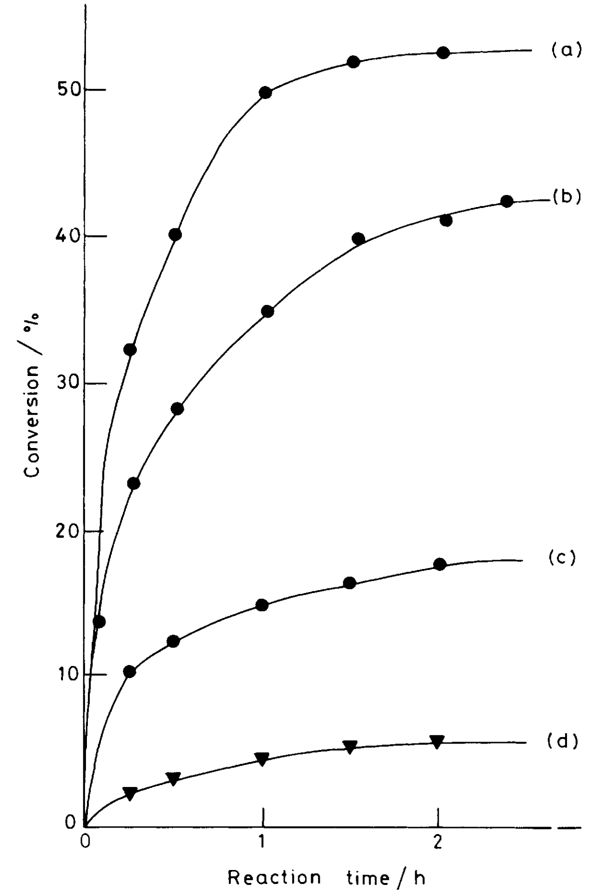

Figure 1. Conversion as a function of reaction time for 3 wt% Re_2O_7 supported on silica–alumina and alumina. (a) HA–, (b) LAH–, (c) LAL–silica–alumina, and (d) γ-alumina.

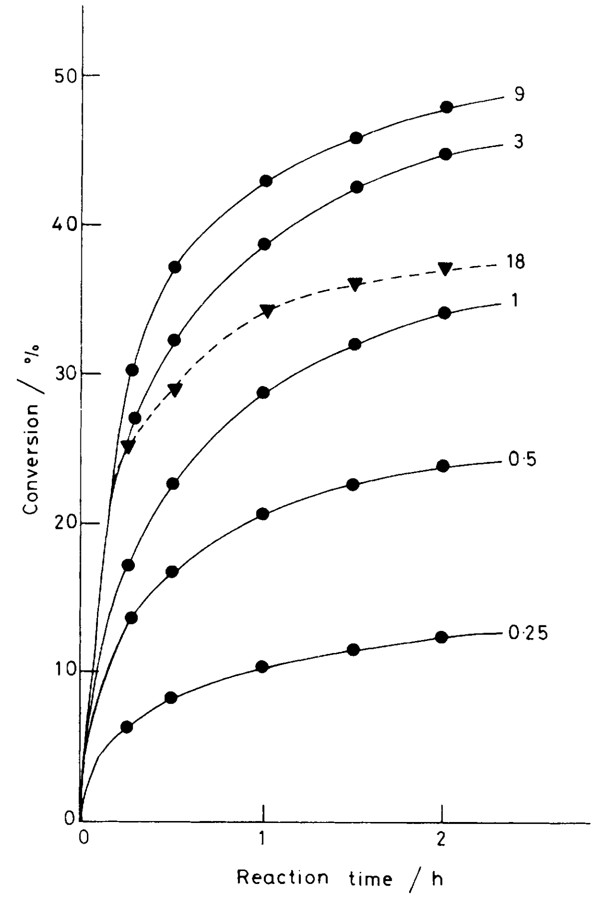

Figure 2. Conversion as a function of reaction time for 18 wt% Re_2O_7/Al_2O_3 catalyst and $Re_2O_7/SiO_2{\cdot}Al_2O_3$–HA catalysts of different Re_2O_7 wt%: ● silica–alumina-supported catalysts; ▼ γ-alumina-supported catalyst. The numbers after the curves are wt% of Re_2O_7.

Figure 1 shows the conversion as a function of reaction time for 3 wt% Re_2O_7 catalysts supported on $SiO_2{\cdot}Al_2O_3$–HA, –LAL, and –LAH, and γ-Al_2O_3, respectively. It appears that silica–alumina-supported catalysts are much more active than alumina-supported ones. HA silica–alumina is a better support than the LAL or LAH silica–alumina. Compared with catalysts supported on alumina, silica–alumina-supported catalysts have a comparable selectivity at a comparable conversion. Compared with ternary oxide catalysts[8] with comparable rhenium loading, silica–alumina-supported catalysts show higher activities and turnover frequencies.

Figure 2 shows the conversions as a function of reaction time for 0.25, 0.5, 1, 3, and 9 wt% Re_2O_7 on $SiO_2{\cdot}Al_2O_3$–HA catalysts and for an 18 wt% Re_2O_7/Al_2O_3 catalyst. In the experiments a double amount of substrate (500 μl) was used; the amounts of catalyst and co-catalyst were the same as in Figure 1. It appears that 3 wt% Re_2O_7 on HA silica–alumina is more active than 18 wt% Re_2O_7 on alumina. It is surprising that even a catalyst with 0.25 wt% Re_2O_7 shows a substantial activity, since alumina-supported catalysts with such low rhenium loadings show only negligible activity.[7,10] Its turnover frequency (0.22 mol s^{-1} per rhenium atom) is *ca.* 18 times that of 18 wt% Re_2O_7 on alumina catalyst.

A 6 wt% Re_2O_7/SiO_2 catalyst was tested under the same conditions; hardly any conversion was observed after several hours. Visual observation showed that 3 wt% Re_2O_7 on LAL silica–alumina and 6 wt% Re_2O_7 on silica were pale yellow and almost white, respectively, after activation and the addition of tetraethyltin, while 3 wt% Re_2O_7 on alumina and on HA or LAH silica–alumina were reddish-brown after the same pretreatment. This implies a difference in the nature of rhenium species retained on the different supports.

Silica–alumina is well known for its specific acidic properties.[9] We think, therefore, the pronounced activity of the silica–alumina supported catalysts is due to their higher acidity, and more specially to their Brönsted acidity. *In situ* Fourier transform i.r. measurements showed that 3 wt% Re_2O_7/Al_2O_3 has no Brönsted acidity as shown by the absence of a 1540 cm^{-1} peak after activation and pyridine adsorption,[11] while silica–alumina-supported 3 wt% Re_2O_7 catalysts do.[12] According to Nakamura *et al.* surface acidity has a beneficial effect on the overall activity for distinct oxide metathesis catalysts.[10] Laverty *et al.*[13] suggested that the donation of protons from surface hydroxyl groups leads to the generation of hydrido-metal complexes which promote the formation of metallacarbene species, an accepted chain-carrying intermediate for metathesis. In line with our view, Ellison *et al.*[7] observed negligible activity of several 5 wt% Re_2O_7/Al_2O_3–$SnMe_4$ catalysts on various alumina supports, except for one distinct catalyst that possessed at least some acidity at that loading.

In our opinion, the difference in catalytic activities between the catalysts supported on HA and on the other silica–alumina samples can be caused by either a difference in Brönsted acidity or a difference in alumina contents. Moreover the different surface areas might be important in this respect. It is known that HA silica–alumina has many more Brönsted acid sites per gram and higher surface area than LAL silica–alumina. LAH silica–alumina has a higher surface area than HA silica–alumina, but lower Al_2O_3 wt%, while in our experiments catalysts based on this carrier showed less activity for the metathesis of methyl oleate. Thus the alumina content seems to be a more important factor with respect to its catalytic activity than is its surface area.

It should be noted that in other catalyst systems the influence of Brönsted acidity is much less pronounced than in rhenia-containing systems. Preliminary results have shown that other co-catalysts besides tetraethyltin (MR_4, M = Sn or Pb; R = Me, Et, or Bu) and other substrates besides methyl oleate (*e.g.* other unsaturated esters, unsaturated nitriles, and propene) exhibit corresponding effects in metathesis experiments with silica–alumina supported catalysts.

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