Activity and stability of laser-photoreduced supported molybdenum oxide metathesis catalysts

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Photoreduction of MoO_3/SiO_2 and $MoO_3/SiO_2 \cdot Al_2O_3$ catalysts in CO with a laser beam at 308 nm resulted, after addition of cyclopropane to form the active sites, in a high activity for alkene metathesis. Both catalyst systems are active for normal alkenes, e.g. propene, and for functionalized alkenes, e.g. methyl oleate, already at room temperature.

Keywords: Metathesis; alkenes; photoreduction; laser; molybdenum oxide; silica; silica–alumina

1. Introduction

A large number of solid catalysts has been reported to be active in the metathesis of alkenes. The most successful catalysts are those based on rhenium, molybdenum and tungsten [1]. Of these, Re_2O_7 supported on alumina or silica–alumina are the most interesting ones because they are already highly active and selective at room temperature. Their activity can even be enhanced by modification of the catalyst with an alkyltin or alkyllead compound [2]. In the latter case they also exhibit activity for the metathesis of functionalized alkenes [3].

Rhenium is, however, a precious metal and the use of a tin compound has several drawbacks: it is toxic, during catalyst regeneration tin oxide is formed which can decrease the catalyst activity [4], while during liquid-phase metathesis tin compounds may leave the catalyst and might appear in the reaction products. Therefore, a catalyst which does not need such a toxic promoter is desirable.

Recently, a very active catalyst system for alkene metathesis has been reported, viz. a MoO_3/SiO_2 catalyst, which is photoreduced in a CO atmosphere with a mercury lamp, and subsequently treated with cyclopropane [5–7]. The catalytic system thus obtained also appeared to be active in the metathesis of functionally substituted alkenes, such as ethyl oleate [8]. It was deduced that during the photoreduc-

tion in a CO atmosphere Mo^{6+} species are selectively reduced to coordinatively unsaturated Mo^{4+} ions; the subsequent addition of cyclopropane induces metal-carbene formation [5–7]. These metal-carbenes form the active site in the metathesis reaction.

We have developed an alternative activation procedure, consisting of CO-photoreduction by a laser beam of 308 nm, followed by the cyclopropane treatment. The wavelength of 308 nm was chosen because the UV–VIS spectrum shows a strong absorption band around 300 nm. This band can be attributed to an electron-transfer process, which is necessary for the reduction of Mo^{6+} [9]. We tested the silica-supported MoO_3 catalyst for both the metathesis of propene and of methyl oleate (*Z*-methyl 9-octadecenoate). The latter compound is used as a model substrate for the metathesis of functionalized alkenes:

$$2\,CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_3 \rightleftharpoons CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3 + CH_3O_2C(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_3\,.$$

We studied the effect of the activation procedure on the catalyst activity for the MoO_3/SiO_2 catalyst as a function of its molybdenum content.

Next, we applied our activation procedure to another catalyst system, viz. MoO_3 on a silica–alumina support. The results were compared with the more conventional promoted alumina- and silica–alumina-supported Re_2O_7 catalysts.

2. Experimental

2.1. CATALYST PREPARATION

The supported MoO_3 catalysts were prepared by pore-volume impregnation of the support material (particle size 180–250 μm). The silica support (Davison Grace 62, BET surface area 325 m^2/g), the alumina support (γ-alumina, Akzo CK-300, BET surface area 208 m^2/g) and the silica–alumina support (Akzo, type HA, 24 wt% Al_2O_3, BET surface area 380 m^2/g) were impregnated with a calculated amount of an aqueous solution of ammonium paramolybdate, followed by drying in air at 383 K. The weight percentages of MoO_3 in the catalysts after calcination were determined by ICP-AES. The supported Re_2O_7 catalysts were prepared as described elsewhere [10].

2.2. ACTIVATION PROCEDURE

The dried catalysts were calcined in a quartz microcatalytic fixed-bed flow reactor by heating them to 773 K in an oxygen stream (50 ml/min) at a rate of 10 K/min. After 2 h in an oxygen stream at 773 K the catalyst was purged with nitrogen for 15 min at the same temperature and subsequently cooled to room temperature.

The calcination of the supported Re_2O_7 catalysts was performed at 823 K by a similar procedure.

After calcination the MoO_3 catalyst was photoreduced at room temperature. During the photoreduction the catalyst was irradiated with a laser beam (Lumonics TE-860-4 Eximer laser, XeCl 308 nm, pulse width 10 ns) for 2–5 min while the catalyst bed was fluidized by a stream of 1% CO in argon. In our procedure the catalyst was exposed to only a fraction (approximately 10%) of the laser beam, which had a power of 2 W. After the photoreduction the CO adsorbed on the catalyst was stripped off in a nitrogen stream at 473 K. The catalyst was subsequently cooled to room temperature and a pulse of cyclopropane (UCAR, grade 2.0) of 8.06×10^{-5} mol was led over the catalyst.

The Re_2O_7/Al_2O_3 catalyst was treated with a tetra-alkyltin compound after calcination.

2.3. ACTIVITY MEASUREMENTS

The activity of the catalysts for the metathesis of propene was tested in the same microflow reactor as used for the catalyst activation procedure, at a propene pressure of 1.5 bar and a reaction temperature of 295 K, as described elsewhere [4].

To test the performance of the catalyst in the metathesis of methyl oleate (prepared as described in ref. [10]), the laser-reduced and cyclopropane-treated MoO_3 catalyst was transferred into a glass batch reactor of 30 ml capacity. The metathesis reactions were carried out in an argon atmosphere at room temperature. In a typical experiment 100 mg of catalyst, 2 ml (5.8×10^{-3} mol) of methyl oleate and 4 ml of hexane (solvent) were used. In the experiment with a 3 wt% $Re_2O_7/SiO_2{\cdot}Al_2O_3$ catalyst, tetrabutyltin was used as the promoter in a molar ratio $Re_2O_7/Sn(C_4H_9)_4$ of 1/1.1; the promoter was introduced prior to the addition of methyl oleate. The reaction was monitored by GC analysis [10].

3. Results

Fig. 1 shows the activity of some CO-photoreduced cyclopropane-treated supported molybdenum oxide catalysts for the metathesis of propene as a function of process time. It can be seen that when the MoO_3 loading is increased, for both the silica- and silica–alumina-supported catalysts the stability of the catalyst also increases. However, the stability of a 7 wt% MoO_3/SiO_2 catalyst appeared to be less than that of a 5 wt% MoO_3/SiO_2 catalyst (not shown). It follows that the silica–alumina-supported catalyst shows a much higher stability than the silica-supported catalysts.

Without cyclopropane treatment the catalysts showed a low activity for only a few hours. A 5 wt% MoO_3/Al_2O_3 catalyst did not show any significant activity.

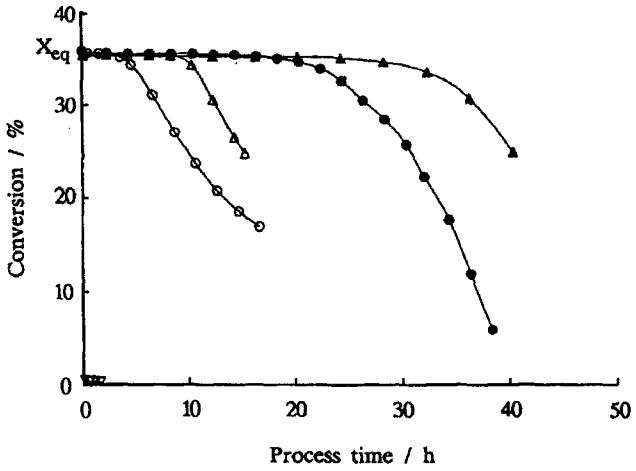

Fig. 1. Conversion of propene as a function of process time at $W/F = 3.5$ kg s/mol (W = weight of catalyst, F = molar propene flow) for CO-photoreduced cyclopropane-treated supported MoO_3 catalysts (100 mg). (○) 1 wt% MoO_3/SiO_2, (●) 1 wt% $MoO_3/SiO_2{\cdot}Al_2O_3$, (△) 5 wt% MoO_3/SiO_2, (▲) 5 wt% $MoO_3/SiO_2{\cdot}Al_2O_3$, (▽) 5 wt% MoO_3/Al_2O_3. Reaction temperature 295 K.

Fig. 2 shows that when a double amount of the $MoO_3/SiO_2{\cdot}Al_2O_3$ catalyst was used, and the contact time (W/F) was kept constant, i.e. a propene flow twice as high, the stability of the MoO_3 catalyst was higher. It also appeared that, within certain limits, the catalyst stability was hardly dependent on the W/F ratio [11]. From fig. 2 it also follows that the stability of a photoreduced cyclopropane-treated 5 wt% $MoO_3/SiO_2{\cdot}Al_2O_3$ catalyst is considerably better than that of a 12 wt%

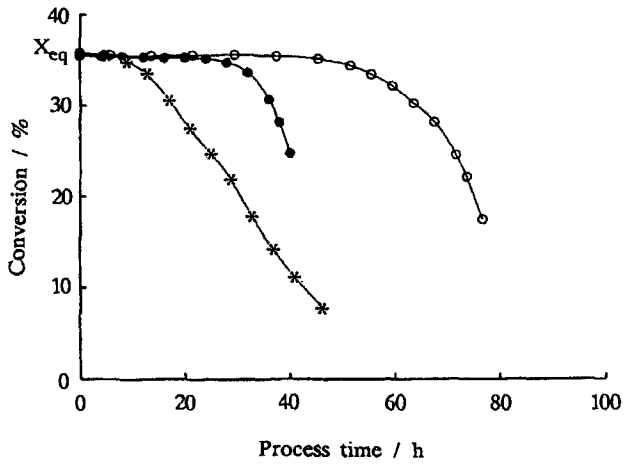

Fig. 2. Conversion of propene as a function of process time at $W/F = 3.5$ kg s/mol for CO-photoreduced cyclopropane-treated 5 wt% $MoO_3/SiO_2{\cdot}Al_2O_3$ catalysts: (●) 100 mg, (○) 200 mg, and for tetraethyltin-promoted 12 wt% Re_2O_7/Al_2O_3 (Re : Sn = 4 : 1), 200 mg: (*). Reaction temperature 295 K.

Re_2O_7/Al_2O_3–$Sn(C_2H_5)_4$ catalyst (Re : Sn molar ratio = 4 : 1) [12], the conventional catalyst for the metathesis of propene.

Fig. 3 compares the activities of different supported MoO_3 catalysts with the activity of 3 wt% Re_2O_7/SiO_2·Al_2O_3–$Sn(C_4H_9)_4$ in the metathesis of methyl oleate. Note that the equilibrium conversion is 50%. It can be concluded that the MoO_3/SiO_2 catalysts are more active per unit weight of catalyst than the SiO_2·Al_2O_3-supported MoO_3 catalyst, and much more active than the rhenium-based catalyst. It was calculated that the turnover number of the photoreduced, cyclopropane-treated MoO_3/SiO_2 catalysts decreases with increasing molybdenum loading.

It should be noted that the optimal activation procedure (photoreduction time, applied laser power and amount of cyclopropane) depends on the molybdenum content of the catalyst. This will be discussed elsewhere.

4. Discussion and conclusions

Photoreduction of the MoO_3/SiO_2 catalysts in CO with a laser beam at 308 nm for only a few minutes resulted, after addition of cyclopropane to form active sites, in a high activity for the metathesis of propene. This activity is at least as high as when the MoO_3/SiO_2 catalyst is reduced by using a Hg lamp [7]. When the same amount of catalyst was used, the 5 wt% MoO_3/SiO_2 catalyst showed an activity in the metathesis of propene comparable to that of a conventional (promoted) 12 wt% Re_2O_7/γ-Al_2O_3 catalyst.

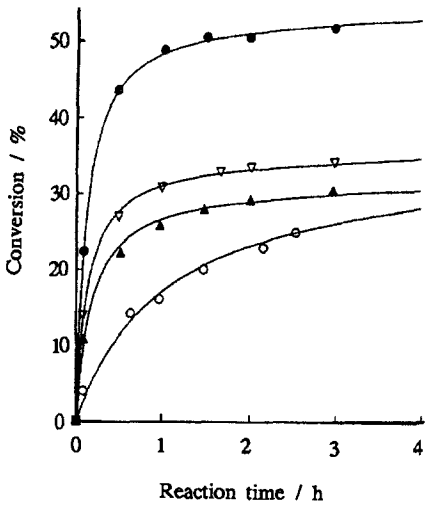

Fig. 3. Conversion of methyl oleate as a function of reaction time for supported CO-photoreduced cyclopropane-treated catalysts compared to a supported rhenium oxide catalyst. (▽) 1.0 wt% MoO_3/SiO_2, (●) 2.5 wt% MoO_3/SiO_2, (▲) 2.5 wt% MoO_3/SiO_2·Al_2O_3 and (○) 3 wt% Re_2O_7/SiO_2·Al_2O_3–$Sn(C_4H_9)_4$. Reaction temperature 295 K.

The same photoreduction procedure applied to a $MoO_3/SiO_2 \cdot Al_2O_3$ catalyst resulted in a catalyst for this reaction with even a much higher activity. The higher activity (or stability) per metal atom in the molybdenum catalyst compared to the rhenium catalyst can be ascribed to the formation of more active sites in the former case.

An enhanced stability of the supported MoO_3 catalysts when the amount of catalyst is doubled can be explained by the presence of a deactivation mechanism which is nearly independent of the propene flow, e.g. isomerisation of the Mo–cyclobutane complex formed in the interaction of the $Mo{=}CH_2$ carbenes with an alkene into an inactive π-complex of the alkene [13].

In the metathesis of methyl oleate the CO-photoreduced, cyclopropane-treated MoO_3/SiO_2 catalysts were more active than a 3 wt% $Re_2O_7/SiO_2 \cdot Al_2O_3$ catalyst promoted with tetrabutyltin, one of the most active catalysts known so far for the metathesis of functionally substituted olefins [3]. Here, the $MoO_3/SiO_2 \cdot Al_2O_3$ catalyst is less active, which is tentatively attributed to complexation of the ester groups to the acidic hydroxyl groups present on silica–alumina, which may block active sites for metathesis.

It can be concluded that the laser-induced activation procedure here described shows promising results for obtaining highly active metathesis catalysts.

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