The identification of different active sites on Mo/Al_2O_3 metathesis catalysts

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Mo/Al_2O_3 catalysts prepared via fixation of $Mo(\eta^3\text{-}C_3H_5)_4$ on Al_2O_3 or by conventional impregnation (2.2 or 2.9 wt% Mo) have been compared with regard to their catalytic behavior in the metathesis of propene in different temperature ranges (293–323 K, 473 K). Different active sites have been distinguished. A site derived from a Mo(VI) precursor by thermal activation in inert gas exhibits stable activity, with a propene reaction order near 1. Other sites that are derived from a reduced Mo precursor, probably Mo(IV), are of higher activity but unstable with time-on-stream and also at elevated temperatures (>323 K). These sites support the metathesis at a propene reaction order of 0.5 and with activation energies between 10 and 25 kJ/mol depending on unknown structural details. Due to their instability, they cannot contribute to the high-temperature ($T > 373$ K) metathesis activity observed with Mo/Al_2O_3 catalysts. The latter is supported by Mo(VI)-derived sites or, at after reduction of catalysts with higher Mo contents, by Mo(IV)-derived sites that are different from those identified in the present study.

KEY WORDS: metathesis; propene; molybdenum; alumina; active sites.

1. Introduction

Olefin metathesis is a hydrocarbon reaction of high scientific interest and practical impact [1,2]. The scientific significance of metathesis is related to the fact that it discloses well the interrelations between homogeneous and heterogeneous catalysis. The reaction mechanism generally accepted for heterogeneous metathesis catalysts has been proposed [3] and substantiated in research with homogeneous catalysts (e.g. [1,2]). There are now several approaches for the preparation of supported Mo metathesis catalysts for which a high homogeneity of structural and catalytic properties of the Mo sites have been claimed. These include systems based on the fixation of Mo allyl complexes on SiO_2 or Al_2O_3, with or without subsequent redox treatments [4–6], or on the photoreduction of Mo/SiO_2 catalysts in CO [7–10]. This knowledge provides a promising basis for an attempt to move Mo metathesis catalysts into the scope of surface science by applying such approaches to the preparation of Mo–organic species on ordered planar oxide substrates.

The present paper arises from a project dealing with the preparation of Mo/Al_2O_3 model catalysts on porous and ordered planar supports via methods outlined by Iwasawa *et al.* [5,6]. The Al_2O_3 support was chosen due to the availability of well-characterized Al_2O_3 substrates—Al_2O_3/NiAl(110) [11], but recently also Al_2O_3/Cr_2O_3 [12]. The aim of the study reported here is to re-visit Mo/Al_2O_3 materials prepared by the fixation of $Mo(C_3H_5)_4$ on $\gamma\text{-}Al_2O_3$ and to study their behavior in the metathesis of propene. It will be shown that a variety of different active sites is accessible via this route although the role of these sites as models for metathesis sites working under industrially relevant conditions is doubtful.

2. Experimental

$Mo(\eta^3\text{-}C_3H_5)_4$ was prepared via standard procedures [13]. It was fixed onto a $\gamma\text{-}Al_2O_3$ kindly provided by KataLeuna GmbH, Leuna, Germany (BET surface area of 216 m^2/g, previously calcined at 823 K in 20% O_2/N_2 for 2 h and in He for 1 h) from a solution in *n*-pentane by overnight reaction at room temperature. The prepared catalyst was repeatedly washed in *n*-pentane, filtered off, purged in flowing Ar for 2 h and transferred into a glove box. The Mo content determined by AES and from the edge height in XAFS spectra was 2.2 wt%.

For comparison, a conventional Mo/Al_2O_3 catalyst was also studied. It was prepared by impregnation of $\gamma\text{-}Al_2O_3$ (260 m^2/g) with a solution of MoO_3 in NH_4OH (pH ≈ 8) by the incipient wetness technique. Characterization data of this catalyst and its activity for propene metathesis at $T \geq 423$ K are reported elsewhere [14,15]. Its Mo content was 2.9 wt%.

The reactivity of these catalysts for the metathesis of propene was studied in a stainless steel apparatus that permitted the reaction to be carried out in static

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circulation mode (240 ml cycle volume) or, by switching a four-way valve, in continuous flow. The quartz reactor, which was loaded in the glove box with 60–120 mg catalyst, was introduced into the gas circulation system via quick fit couplings. An activated MnO/SiO_2 guard bed kept oxygen traces from the catalyst. Possible leakage problems at critical connections (quick fit and metal–quartz couplings) were avoided by housing the latter in casings flushed with inert gas.

The reaction products were analyzed by on-line gas chromatography. In the batch experiments, the ethene/butene ratio was mostly >1 (up to 1.45, largely between 1.3 and 1.1) and exhibited a decreasing trend with higher time-on-stream, temperature and initial propene partial pressure. This imbalance is probably due to adsorption of butenes on the high-surface-area support because it was not observed under flow conditions. Conversion data given in this paper are based on propene consumption, but were checked via the ethene formation, in particular for low conversions.

3. Results

In figure 1 the reactivity of Mo allyl fixed on Al_2O_3 ("Mo-allyl/Al_2O_3") is compared with that of the conventional Mo/Al_2O_3 catalyst. Figure 1(a) shows that the response of the former on treatments proposed in the earlier work of Iwasawa's group [6] is as described there. The fixed Mo allyl (state A) is an active metathesis catalyst. Upon reduction in H_2 at 868 K (state B), the metathesis activity is strongly suppressed, and it disappears completely when an oxidation in air at 673 K follows the reduction step (⟶ state C). However, when the oxidized catalyst is reduced in hydrogen at 823 K (state D), the metathesis activity reappears again, although the original reaction rates are no longer achieved. In figure 1 turnover frequencies (TOF) derived from the initial rates under the assumption that all Mo atoms participate in the reaction are displayed near the appropriate curves.

In figure 1(b) reactivity data for the conventional catalyst are reported. It has been shown [15] that this type of catalyst has to be activated for the metathesis reaction by a high-temperature treatment in inert gas. This has been confirmed in the present study (see figure 1(b), states A_{673} and A_{973}). After the high-temperature treatment, the catalyst exhibits an activity of the same order of magnitude as Mo-allyl/Al_2O_3 (state A). Although the initial rate is lower despite the higher Mo content, which results in a considerable disadvantage in the TOF, the conversion exceeds that obtained over the fixed Mo allyl after a longer reaction time. This is obviously due to different reaction kinetics. In figure 1(b) the effect of a reduction of the conventional catalyst in hydrogen at 823 K is also reported and compared with

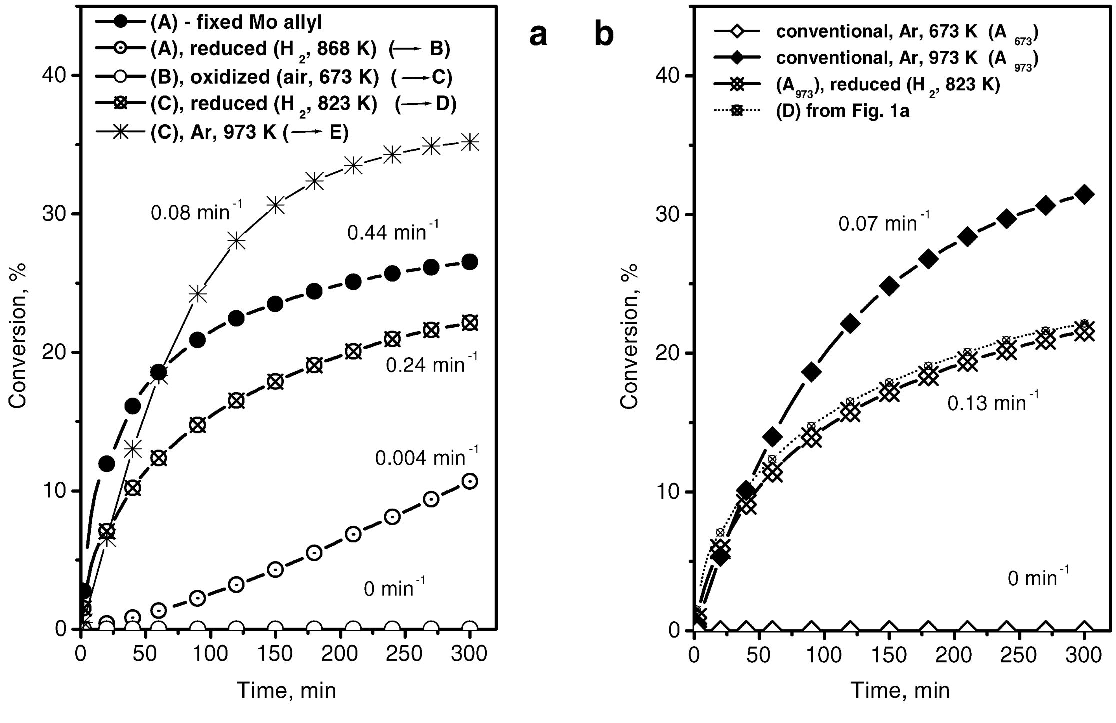


Figure 1. Metathesis activities of Mo-allyl-derived and conventional Mo catalysts. Batch recirculation mode, $T = 298\,K$, $m_{cat} = (67.8 \pm 0.9)$ mg, $p_{0,propene} = 0.092$ bar, turnover frequencies derived from initial rates are indicated in the graphs; all treatment temperatures were established in 10 K/min ramps from room temperature or from the previous temperature, cooling stages in Ar. (a) Catalysts derived from Mo-allyl/Al_2O_3: ●, untreated (A); ⊙, (A) reduced in H_2 at 868 K for 90 min (state B); ○, (B) oxidized in synthetic air at 673 K for 90 min (state C); ⊠, (C) reduced in H_2 at 823 K for 90 min (state D); ∗, (C) treated in Ar at 973 K for 1 h (state E). (b) States of the conventional catalyst: ◇, activated in Ar at 673 K for 1 h (A_{673}); ◆, activated in Ar at 973 K for 1 h (A_{973}); ※, (A_{973}) reduced in H_2 at 823 K for 90 min; ⊗, state D, see figure 1(a).

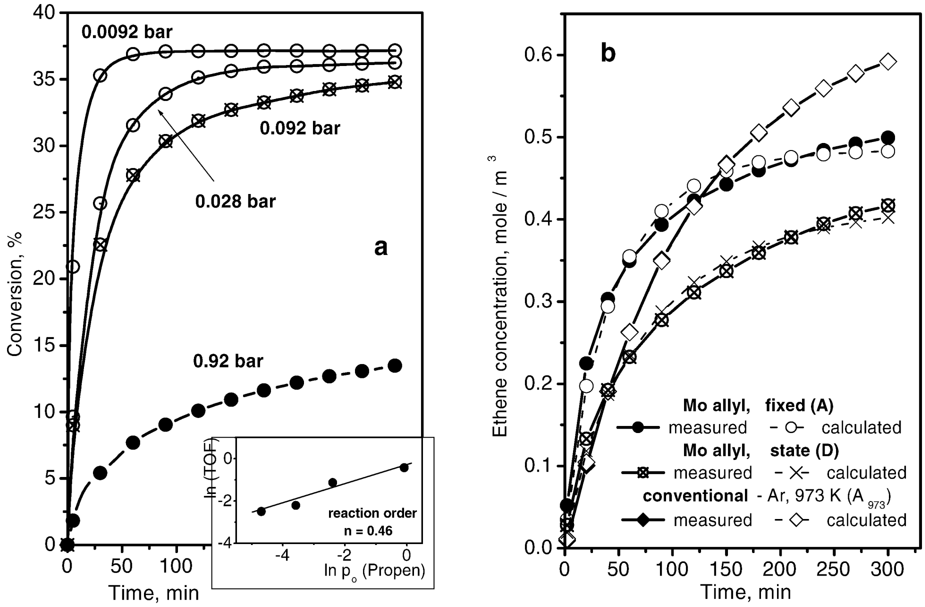


Figure 2. Kinetics of propene metathesis over Mo/Al_2O_3 catalysts. (a) Mo-allyl/Al_2O_3, untreated (A), $T = 298$ K, variation of initial propene pressure, $m_{\mathrm{cat}} = (117.6 \pm 2.1)$ mg. (b) Comparison of measured and calculated conversion curves for Mo-allyl/Al_2O_3, untreated (A), after redox treatment (D) and conventional Mo/Al_2O_3, activated in Ar at 973 K (A_{973}), $T = 298$ K, $m_{\mathrm{cat}} = 66.8$ mg, $p_{0,\mathrm{propene}} = 0.092$ bar. For kinetic parameters, see table 1.

the behavior of Mo-allyl/Al_2O_3 after an analogous activation (state D). The kinetic curves are now almost identical, i.e. the characteristics of the kinetic curve have been completely changed by the reduction. Analogously, the effect of a 973 K inert gas treatment on Mo-allyl/Al_2O_3 after the oxidation step leading to state C was investigated. The resulting curve, which is shown in figure 1(a), is very similar to that obtained with the conventional catalyst after the same treatment, but the overall reactivity of the thermally activated Mo allyl catalyst is higher.

In figure 2 the results obtained so far in the attempt to establish the kinetic rate law of the metathesis reaction over these catalysts are presented. Figure 2(a) shows conversion curves measured upon variation of the initial propene pressure over two orders of magnitude. The weak response of the turnover frequencies on this drastic concentration change indicates that the reaction order in propene will be <1. A logarithmic plot of the turnover frequencies estimated from the initial rates versus the initial propene pressure yields a reaction order of ~ 0.5.

In figure 2(b), the kinetic curves are compared with the best mathematical models found so far. For the conventional catalyst and $T \geq 423$ K, it has been demonstrated [15] that the metathesis kinetics follow a rate law:

$$r = c_{0,\mathrm{propene}}^{n}[k_1(1-X)^n - 0.5k_{-1}X^n] \qquad (1)$$

(k_1, k_{-1} are the rate constants of metathesis and reverse reaction, $c_{0,\mathrm{propene}}$ is the initial propene concentration, X is the propene conversion) with a reaction order $n = 0.8$. The same rate law was assumed for the room-temperature reaction under static recirculation conditions neglecting the slight disparity between ethene and butene. A model with $n = 0.9$ (see table 1) perfectly fitted the kinetic curve found with the conventional catalyst (state A_{973}) up to high conversions (compare figures 2(b), 1(b)). A similar coincidence was obtained with state E of Mo-allyl/Al_2O_3 (i.e. after activating the oxidized form in Ar at 973 K). On the other hand, the attempt to model the conversion curves obtained with Mo-allyl/Al_2O_3 in states A and D up to high conversions resulted in a decrease of the reaction order below that extracted from the initial rates. In the best model n was 0.2 (see table 1), but the coincidence between calculated and measured curves was unsatisfactory: the calculated curves start with a lower initial rate, they exceed the experimental curves after some time, but fall short again at longer reaction time. This behavior is typical for the untreated catalyst (A) as well as for the state after the redox treatment (D). It is obvious that the experimental ethene concentration increases more slowly than would have been expected if the order 0.46 had been applied together with the initial rates observed. From this it may be inferred that a deactivation process

Table 1

Kinetic parameters for the metathesis of propene over Mo/Al_2O_3 catalysts (derived from conversion curves in figure 2(b)) ($T = 298$ K, $m_{\mathrm{cat}} = 66.8$ mg, $p_{0,\mathrm{propene}} = 0.092$ bar)

Catalyst	n	k_1[a]	k_{-1}[a]
Conventional (A_{973})	0.9	0.56	2.55
Mo-allyl/Al_2O_3, initial (A)	0.2	10.86	15.23
Mo-allyl/Al_2O_3, after redox treatment (D)	0.2	5.64	8.35

[a] In $\mathrm{mol}^{(1-n)}\,\mathrm{m}^{3n}\,\mathrm{kg}^{-1}\,\mathrm{h}^{-1}$.

may be superimposed upon the reaction kinetics for A and D.

This is confirmed by flow experiments with the Mo/Al$_2$O$_3$ catalyst in different states, the results of which are reported in figure 3. Over the initial Mo-allyl/Al$_2$O$_3$ catalyst (state A), the propene conversion evaluated from ethene formation decreased from 1.1 to 0.35% over a period of 5 h. The experiments with catalyst states obtained by thermal inert gas treatment of oxidized Mo/Al$_2$O$_3$ have been performed at 473 K, at which temperature the propene conversions with Mo-allyl/Al$_2$O$_3$ in states A and D were negligible (see also below). With these catalysts on the basis of oxidized Mo, conversions near the equilibrium ($x_\infty = 0.4$) are obtained with the W/F applied, and instead of a deactivation the propene conversion is constant over several hours after a short induction period.

In figure 4 it is demonstrated that the metathesis activity of the fixed Mo-allyl/Al$_2$O$_3$ can be easily improved by a low-temperature hydrogen treatment. The data points in figure 4(a) were collected in consecutive metathesis experiments with a batch of Mo-allyl/Al$_2$O$_3$ (states A) at 298 K and with a duration of 20 min, with intermittent treatment of the catalyst in Ar or H$_2$ for 1 h at the temperatures indicated. With the Ar treatment, the propene conversions indeed decrease up to a treatment temperature of 323 K. At

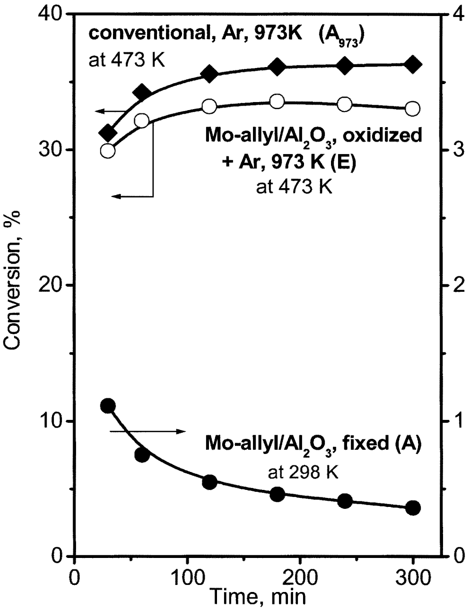


Figure 3. Stability of metathesis activity in different states of Mo/Al$_2$O$_3$ catalysts. Flow reactor measurements with undiluted propene. ●, Mo-allyl/Al$_2$O$_3$, untreated (A), $T = 298$ K, W/F = 5 kg s/mol; ◆, conventional Mo/Al$_2$O$_3$, after Ar, 973 K (A$_{973}$), $T = 473$ K, W/F = 7.5 kg s/mol; ○, Mo-allyl/Al$_2$O$_3$, state (E), activation in Ar at 973 K after oxidation step (D), $T = 473$ K, W/F = 7.5 kg s/mol.

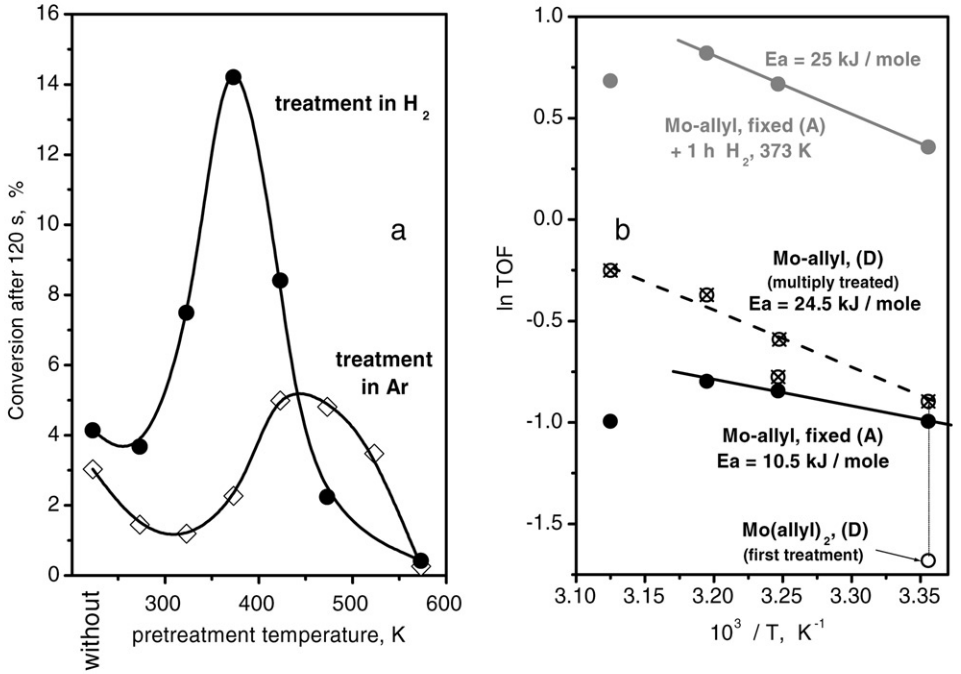


Figure 4. Activation of Mo-allyl sites by hydrogen treatment. (a) Dependence of initial reaction rate of Mo-allyl/Al$_2$O$_3$ on the temperature of treatment in H$_2$ or Ar. Measurement conditions: batch recirculation mode, $T = 298$ K, $m_{\text{cat}} = 59.1$ mg (Ar experiment) or 80.2 mg (H$_2$ experiment), $p_{0,\text{propene}} = 0.060$ bar, initial rate derived from conversion after 2 min (at overall reaction time of 20 min); treatment conditions: 1 h at the temperatures indicated, consecutively, with interchange of reaction and treatment steps, starting at low temperatures. (b) Temperature dependence of initial reaction rates over Mo/Al$_2$O$_3$ catalysts; reaction conditions: $m_{\text{cat}} = (67.8 \pm 0.9)$ mg, $p_{0,\text{propene}} = 0.060$ bar. ●, Mo-allyl/Al$_2$O$_3$, untreated (A); ○, Mo-allyl/Al$_2$O$_3$, after redox treatment, first experiment (state D); ⊠, (C) reduced in H$_2$ at 823 K for 90 min (state D); ⊠, Mo-allyl/Al$_2$O$_3$ (state D) after multiple redox cycles; ●, Mo-allyl/Al$_2$O$_3$, after 1 h H$_2$ treatment at 373 K.

higher temperatures, however, the conversions go through a maximum, exceeding by far the value of the initial catalyst despite the considerable duration of the experiment. This shows that any deactivation phenomena demonstrated in this paper are not due to oxygen leakage problems in the experimental setup used. With the same experimental procedure, the initial propene conversion increased by 350% after reduction in hydrogen at 373 K. In experiments with direct reduction at 373 K (1 h, after 20 min activity test with the initial sample), the initial metathesis rate typically increased by 400%.

Figure 4(b) summarizes information available about the temperature dependence of the metathesis activity of Mo-allyl/Al_2O_3 in various states. The turnover numbers reported were estimated from propene conversions after 2 min. Different activation energies were obtained for the fixed Mo-allyl/Al_2O_3 (state A, 10.5 kJ/mol) and for the state obtained from this by treatment in H_2 at 373 K (25 kJ/mol). Since the higher activation energy occurs with the more active catalyst, this observation should not arise from a transport limitation; hence, it strongly suggests structural differences between the sites in the catalyst states compared. For state D obtained by redox activation, we noted that in repetitive experiments, where the catalyst was regenerated by oxidation at 673 K and reduction at 823 K, the metathesis activity increased considerably and approached that of the fixed Mo-allyl/Al_2O_3 (see arrow in figure 4(b)). With such catalysts subjected to a multiple redox activation, an activation energy of ~25 kJ/mol was found as well.

The most significant result is that the initial catalyst and that obtained by H_2 treatment of Mo-allyl/Al_2O_3 lose their activity above 313 K. The sites produced by the redox treatment (state D) are somewhat more stable, but in a measurement at 473 K, the TOF was found to be still the same as at room temperature, i.e. most of the original sites should have lost their activity at this temperature [16]. In a flow experiment at 473 K ($W/F = 7.5$ kg s/mol, i.e. analogous to the flow experiments with the Mo(VI)-derived states, cf. figure 3) the catalyst obtained by redox treatment of Mo-allyl/Al_2O_3 (state D) achieved a conversion of 0.16%, which decreased to 0.03% in 5 h [16].

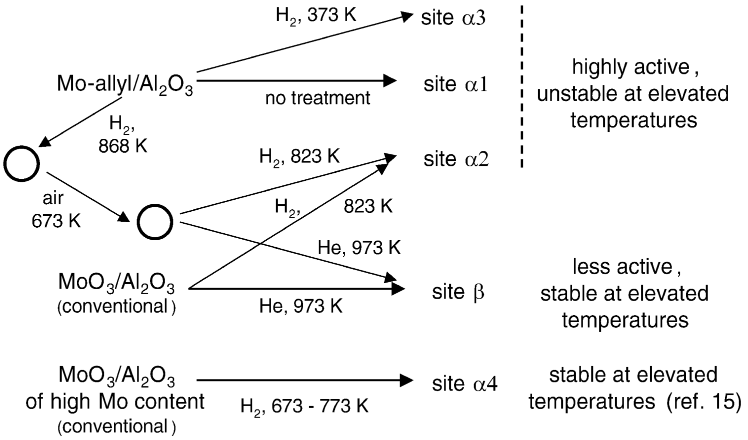
4. Discussion

The reactivity data presented above show that our preparation has led to catalysts comparable with those described by Iwasawa's group [5,6,17]. Using the kinetic data reported in figure 2 for extrapolation of our data on their typical reaction conditions (273 K, 20 torr propene) yields a TOF of 0.17 min^{-1} while a value of 0.3 was reported previously [17]. Possible reasons for the remaining difference are being studied, but it has been pointed out [6] that the reactivity of the sites obtained may depend on the alumina employed. The reaction order and the activation energies measured coincide well with the previous data ($n = 0.5$, $E_a = 8$ kJ/mol). It has been reported [17] that the activity of the fixed Mo-allyl/Al_2O_3 can be strongly enhanced by thermo-evacuation at 423 K. We found that a hydrogen treatment at 373 K has a similar effect (figure 4), which is, however, accompanied by a drastic increase in the activation energy to values above those reported elsewhere [6,17] for Mo/Al_2O_3 catalysts.

The response of the metathesis rate to the treatments suggested [5,6] to produce Mo(IV) oxo sites of high structural homogeneity on the whole agrees with expectations. There is, however, some residual metathesis activity after reduction at 868 K. The turnover frequency of the final reduced Mo oxo state (D) initially deviates significantly from that of the untreated Mo-allyl site while it was reported by others to be almost identical [5,6]. However, the catalyst changes when redox cycles are performed with it, which results in a considerable gain in metathesis activity. For this reason, the activation energy of 25 kJ/mol reported for this catalyst (cf. figure 4(b)) is subject to some uncertainty since it is not clear if the catalyst state was identical in all measurements included in the series. While investigations on the origin of these changes are in progress, our observations of an activation by redox cycling suggest that the reduction step does not proceed selectively but leads to mixed valence states. Such a conclusion was suggested by Aigler *et al.* in an XPS study with Mo-allyl sites fixed on SiO_2 [18]. We have also tried to use the alternative route to alumina-supported Mo(IV) oxo species (state $B + O_2$, 273 K [5,6]), but found it to be of low reproducibility.

Remarkably, the catalytic activity of the sites produced via procedures suggested by Iwaswa's group is not stable with time-on-stream and temperature increase. The latter shows that the sites are not homogeneous in their properties, and possibly also in their structure, since there are sites that work at higher temperatures while other sites do not tolerate them. This applies already to the initial catalyst, the fixed Mo allyl complex.

As to the conventional catalyst, we agree with earlier findings that its initial activity is lower than that of Mo-allyl-derived sites, but it is of the same order of magnitude. Due to its stability properties, the conventional catalyst provides the higher propene conversions at higher reaction times. There are quite obvious differences between the sites of the conventional and of the Mo-allyl-derived catalyst. The former operate at different reaction kinetics: the propene reaction order of propene is 0.9, the activation energy, which has not been reproduced in the present study, is 35 kJ/mol according to Grünert *et al.* [15], the sites are completely stable with time-on-stream and temperature increase. The most significant result of the present work is, however, that the two types of sites—active, but unstable



Scheme 1. Treatments and metathesis sites.

(α) and less active but stable (β)—can occur both on the Mo-allyl-based and on the conventional catalyst. Oxidation of the Mo-allyl sites with subsequent high-temperature Ar treatment produces "α sites" while reduction of "α sites" on the conventional catalyst produces "β sites". From this it can be concluded that the properties of the different sites are not related to the preparation process (via allyl fixation or conventional) but to the oxidation state of the Mo oxo precursor species. That from which the "α sites" are formed is (formally) in the +6 state while the precursor of the "β sites" is more reduced, probably Mo(IV). Moreover, it may be suggested that the fixed Mo allyl sites lose their particular properties, which according to Iwasawa *et al.* [5,6] should enable them to undergo discrete redox steps, together with their ligands. There is no qualitative difference in the properties of the resulting metathesis sites irrespective of whether a Mo-allyl-derived or a conventional Mo(VI)/Al_2O_3 catalyst is thermally activated in Ar or reduced in H_2. The somewhat higher activities of the Mo-allyl-derived catalysts imply, however, that the allyl route provides a better dispersion of the Mo species on the alumina. A similar conclusion has been implicitly drawn by Aigler *et al.* who used the Mo-allyl route to prepare Mo(VI)/SiO_2 precursors for further activation by photoreduction in CO [10,19].

As a result, several types of metathesis sites may be distinguished on Mo/Al_2O_3 catalysts (cf. scheme 1). There are those derived from reduced Mo precursors, probably Mo(IV), which are highly active but not stable. As indicated by the different activation energies (cf. figure 4(b)), these sites have different properties obviously depending on changes in the Mo coordination sphere, which arise from the pretreatments applied (H_2, 373 K, full redox cycle, or none). In addition, there are sites originating from Mo(VI) precursors, which have to be activated by thermal treatment in inert gas at high temperatures. The formation of these sites is subject to further studies. The fact that the precursor has to be Mo(VI) (no reduction during thermal treatment in Ar was found in preliminary XPS and XAFS studies [20]) does not necessarily mean that this is the Mo oxidation state also after the formation of the metathesis site. This site obviously supports the metathesis activity exhibited by Mo/Al_2O_3 catalysts of low Mo content at higher temperatures. On the other hand, it is known that at higher Mo contents, the metathesis activity of Mo/Al_2O_3 may be improved by reduction at 673–823 K, and the excess activity, which is stable at temperatures above 423 K, has been assigned to a Mo(IV) site [15]. This Mo(IV) site is obviously different from those on Mo/Al_2O_3 catalysts of low Mo content. While the latter sites are probably isolated, the former should be part of oligomeric surface molybdate species present at higher Mo contents. The predominant formation of reduced Mo metathesis sites from oligomeric entities has been proposed recently from results obtained with Mo/alumosilicate metathesis catalysts [21].

5. Conclusions

In Mo/Al_2O_3 catalysts of low Mo content, several active sites for the metathesis of propene may be distinguished, which are derived from Mo in different oxidation states. A site derived from a Mo(VI) precursor supports the metathesis reaction over a broad temperature range, with a propene reaction order near 1 and an activation energy of ~35 kJ/mol. The description of these sites, in particular the Mo oxidation states in them, is a challenge for future research. Other sites, which are derived from reduced Mo, probably Mo(IV) (e.g. by fixation of $Mo(\eta^3\text{-}C_3H_5)_4$ on Al_2O_3, by specified pretreatments of the latter or by reduction of Mo(VI)/Al_2O_3), are more active but not stable, and their structural homogeneity is doubtful. They catalyze the metathesis with a reaction order of 0.5 and an activation energy that ranges from 10 to 25 kJ/mol depending on unknown structural details. These sites cannot operate at $T \geq 473$ K, and they are therefore different from Mo(IV)-derived sites that have been shown in the literature to contribute to the metathesis activity of Mo catalysts with high Mo content.

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