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Active Centers for the Metathesis and Isomerization of Alkenes on Tungsten-Oxide/Silica Catalysts

A. J. VAN ROOSMALEN[1] AND J. C. MOL

Institute for Chemical Technology, University of Amsterdam, Plantage Muidergracht 30,
1018 TV Amsterdam, The Netherlands

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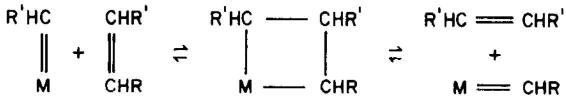
Tungsten-oxide/silica catalysts from various preparations were compared for their activity in the metathesis of propene and the subsequent isomerization of the 2-butene formed. Catalysts obtained by cogelation of WCl_6 and $Si(OC_2H_5)_4$ were much more active than catalysts prepared by conventional methods. Silylation with hexamethyldisilazane, a specific poison for Brønsted-acidic hydroxyls, caused a 10- to 100-fold increase in the metathesis rate; ammonia treatment had much less effect. The influence of silylation on the isomerization activity depended on the method of catalyst preparation. It is concluded that the isomerization involves a carbenium-ion intermediate. The protons needed to produce this intermediate are thought to be donated by Lewis acid site–alkene complexes, while surface silanols make the gas-phase butene accessible for proton exchange. The generation of active centers for metathesis is explained by proton donation by the Lewis acid site–alkene complexes to tetravalent tungsten compounds. The resulting tungsten hydrides are believed to react with alkene in the way proposed by D. T. Laverty, J. J. Rooney, and A. Stewart [*J. Catal.* **45**, 110 (1976)]. Back-donation of a proton to the Lewis acid complex yields a tungsten carbene, which is the postulated chain initiator. The Lewis acid sites are depicted as coordinatively unsaturated, hexavalent tungsten species bonded by W—O—Si bridges to the silica lattice. The number of ≡Si—O ligands surrounding the tungsten atom is thought to determine the strength of the Lewis acid sites and, hence, the activity of the catalyst. This number can be increased by silylation or by choosing a suitable catalyst preparation method such as cogelation.

INTRODUCTION

Since the first paper on the metathesis of alkenes was published in 1964 (*1*), this catalytic reaction has drawn considerable attention, both from a theoretical and a practical point of view (*2–4*). Currently, it is generally assumed that alkene metathesis is a chain reaction, involving metal–carbene complexes, reversibly reacting with alkenes *via* a metallacyclobutane intermediate: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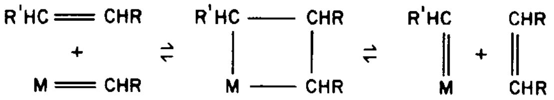
(1b)

The way in which the initial metal–carbenes are formed is still not fully understood, especially not for catalyst systems that do not contain carbon, such as tungsten-oxide/silica and most other solid catalysts. Laverty *et al.* (*5*) presented evidence for an initiation mechanism in which carbenoid species are generated by a β-hydrogen addition of a transition-metal hydride to the alkene, followed by an α-hydrogen elimination:

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[1] Present address: Philips Research Laboratories, 5600 A Eindhoven, The Netherlands.

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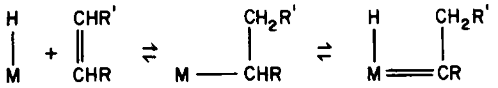
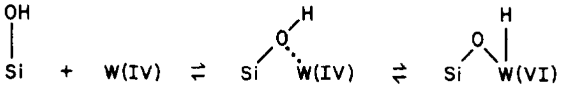


$$\overset{H}{\underset{M}{|}} + \overset{CHR'}{\underset{CHR}{\|}} \rightleftarrows \overset{CH_2R'}{M\text{—}\overset{|}{CHR}} \rightleftarrows \overset{H\quad CH_2R'}{M{=}CR} \quad (2)$$

On solid oxidic catalysts, these hydrides are believed to originate from the interaction of reduced transition-metal ions with Brønsted-acidic surface hydroxyls of the support, e.g.:



$$\overset{OH}{\underset{Si}{|}} + W(IV) \rightleftarrows Si\text{—}\overset{H}{O}\cdots W(IV) \rightleftarrows Si\text{—}O\text{—}\overset{H}{\underset{W(VI)}{|}} \quad (3)$$

However, ammonia and pyridine adsorption experiments have shown that activated tungsten-oxide/silica does not hold strong Brønsted acid sites (*6*). Therefore, if metal hydrides are formed according to Eq. (3), the surface hydroxyls are only weakly acidic.

The metathesis of propene leads to the simultaneous formation of ethene and 2-butene (*cis* and *trans*). Tungsten-oxide/silica also catalyzes the isomerization of alkenes, so that the 2-butene formed reacts further to give 1-butene. This double-bond isomerization is not necessarily associated directly with the active sites for metathesis. Silica itself can be an active isomerization catalyst as well (*7*). On commercial silica gel the activity for butene double-bond isomerization results from a cooperation of aluminum impurities and surface silanols. This isomerization can be greatly suppressed by silylation of the weakly Brønsted-acidic silanols with hexamethyldisilazane, which converts surface hydroxyl groups to trimethylsiloxy groups (*8*):

$$2\text{—}OH + HN(Si(CH_3)_3)_2 \rightarrow 2\text{—}OSi(CH_3)_3 + NH_3. \quad (4)$$

This poisoning appears to leave the Lewis-acidic aluminum sites unaffected (*7, 9*).

Here, we report on the activity for metathesis and isomerization of tungsten-oxide/silica catalysts obtained from various preparations, and on the effect of treatment with hexamethyldisilazane on their catalytic activity. The aim of the silylation was to find out if weakly Brønsted-acidic hydroxyls play a role in the initiation of alkene metathesis, and, if not, whether it is possible to eliminate the double-bond isomerization without affecting the active sites for metathesis.[2] In the reaction of hexamethyldisilazane with surface hydroxyls, ammonia is evolved (Eq. (4)). Because ammonia is known to affect both the isomerization and the metathesis activity of silica-based systems (*11, 12*), we also studied the effect of ammonia treatment. Finally, an attempt is made to postulate for the active sites a model which can account for the results of our kinetic experiments.

EXPERIMENTAL

Materials

The catalysts were prepared by impregnation (WSI: 360 $m^2\ g^{-1}$, 4.2 wt% WO_3), reaction (WSR: 360 $m^2\ g^{-1}$, 5.7 wt% WO_3), or cogelation (WSC: 600 $m^2\ g^{-1}$, 3.7 wt% WO_3) as described in a previous paper (*6*). In the preparation of WSC an extensive washing with methanol is included to convert the initial hydrogel into an alcogel. The reason for this is that the alcogel can be dried by autoclaving, whereas the hydrogel cannot. The high reactivity of water near its critical point would cause the porous structure of the latter to collapse. Because tungsten oxide is slightly soluble in methanol, certain active sites might be leached from the catalyst surface during the methanol treatment. In order to eliminate this effect, a portion of aged hydrogel was taken, dried in air, milled and sieved, and calcined for 4 h at 825 K in dry air. This catalyst will be

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[2] Hexamethyldisilazane has been used by other workers to improve the selectivity of a titania/silica epoxidation catalyst (*10*).

denoted WSCA. It contained about 6 wt% WO_3 and had a surface area of 540 $m^2\ g^{-1}$ (BET nitrogen).

Purified propene was prepared by distilling polymerization-grade propene (Matheson) over alumina, molecular sieves (4A), and copper-on-alumina catalyst. The product was over 99.8% pure, its main contaminant being propane (0.1%).

Equipment and Procedures

The kinetic experiments were carried out in a closed circulation system with a total volume of $25 \times 10^{-5}\ m^3$ (*7*). Typically, 0.5 g of catalyst was activated *in situ* by heating for 1 h at 825 K in a stream of oxygen, followed by evacuation for 1 h at the same temperature, and for 15–18 h at 725 K. After cooling to the reaction temperature (700 K), 1.1×10^5 Pa of propene was admitted to the system and allowed to react for 10 min. During this period one or more samples were withdrawn for GC analysis. Then, the reactor was evacuated for 10 min, and a new batch of propene was introduced. This procedure was repeated three to ten times, after which the system was evacuated and filled with 1.0×10^5 Pa of helium. The circulation pump was started and the reactor cooled to 525 K. At this temperature, 10^{-3} mol of either hexamethyldisilazane or ammonia was injected with a hypodermic syringe and allowed to react for 20 min. Next, the system was evacuated briefly at 525 K, and for 10 min at 700 K, and the activity of the treated catalyst was measured another three to six times.

We restricted ourselves to measurements where the propene conversion was below 10%, so that the reaction rate constant for metathesis, k_m, can be approximated by

$$k_m = x_e/t, \tag{5}$$

where t is the reaction time in seconds and x_e the molar fraction of ethene at time t. The subsequent double-bond isomerization of 2-butene was assumed to be a reversible, first-order reaction with equal rate constants for the formation of 1-butene from *cis*- and *trans*-2-butene. Under these assumptions, and applying Eq. (5), it can be derived that

$$k_i t(1 + K)((1 + K)x_{1b}/x_e - 1) = 1 - \exp\{k_i t(1 + K)\}, \tag{6}$$

where x_{1b} is the molar fraction of 1-butene at time t, k_i the reaction rate constant for 1-butene formation from 2-butene, and K the 2-/1-butene ratio at thermodynamic equilibrium, i.e., 2.75 at 700 K (*13*). k_i was calculated from Eq. (6) using Newton's method.

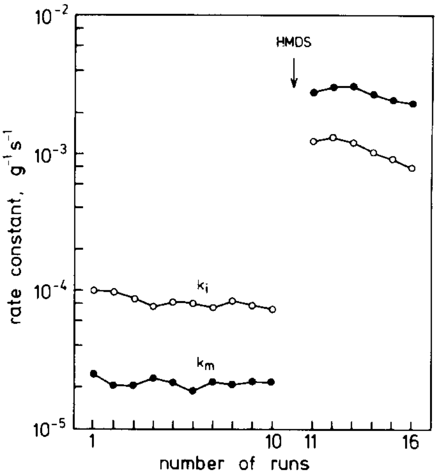


FIG. 1. Typical rate constants for metathesis (●) and isomerization (○) before and after treatment with hexamethyldisilazane (HMDS). Catalyst: WSI, time scale on horizontal axis: 20 min per run; interval between runs 10 and 11: 45 min.

RESULTS

The selectivity of the catalysts towards ethene and butene was better than 99% under the applied conditions; the main side products were butadiene and pentene, and, for the silylated catalyst, methane. The initial *cis*/*trans*-2-butene ratio was near unity in all experiments.

Figure 1 shows a typical example of the variation with time of k_i and k_m before and after hexamethyldisilazane (HMDS) treatment. A summary of the effect of HMDS and ammonia on the activity of all our catalysts is given in Fig. 2.

The values for k_i and k_m given here are

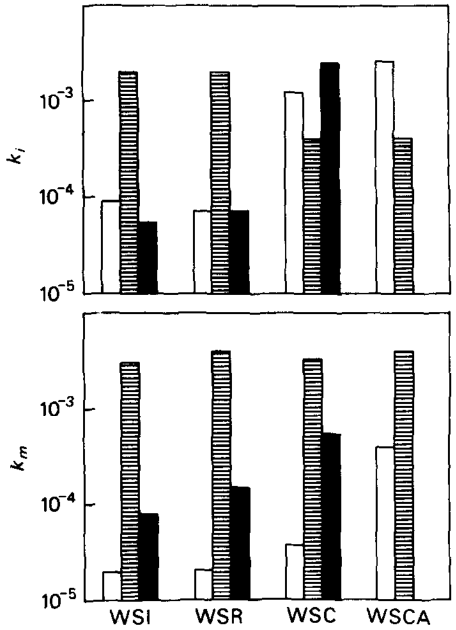


FIG. 2. Rate constants (g^{-1} s^{-1}) for metathesis (k_m) and isomerization (k_i) on various tungsten-oxide/silica catalysts before (white) and after treatment with hexamethyldisilazane (shaded) or ammonia (black).

mean values calculated from either the last three measurements before or the first three after treating the catalysts with the above-mentioned agents. Except for the ammonia-treated samples (see below) the activity showed no trend in either direction over these measurements. The reproducibility of the rate constants was ±30% or better. A blank treatment, i.e., cooling the catalyst to 525 K, flushing with helium, and reheating to 700 K, did not affect k_i and k_m significantly. On first contact with propene, the isomerization activity of some catalyst samples was high when compared with the steady-state value, while the metathesis activity was low. This rather irreproducible effect has not been studied further; no data from such samples are included in Fig. 2. For a description of induction effects (catalyst break-in), see the Discussion section.

It can be seen from Fig. 2 that, before any treatment, WSI and WSR have about the same activity, and that WSC and especially WSCA are more active, both in metathesis and isomerization. The high activity of WSCA relative to WSC indicates that WSC has indeed lost active tungsten during the washing with methanol (see the Experimental section).

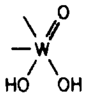
Treatment with hexamethyldisilazane causes a 10- to 100-fold increase in metathesis activity; it lowers k_i on the cogelation catalysts and enhances k_i on the other two catalysts. Treatment with ammonia has little effect on k_i and increases k_m much less than silylation does. The enhancement of the activity for metathesis after ammination was only temporary; k_m decreased ca. 25% per run, in accordance with the observations of Gangwal and Wills (*11*) and Takahashi (*12*). Hence, it appears that the effect of hexamethyldisilazane cannot be explained from the evolution of ammonia in the reaction with surface hydroxyls, and that a separate explanation is needed.

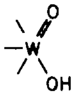
DISCUSSION

Isomerization

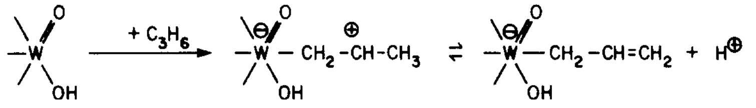
The double-bond isomerization of linear butenes on silica–alumina most probably involves an *s*-butyl carbenium-ion intermediate. The protons producing the ionic intermediate are thought to be donated by monomeric or oligomeric butene irreversibly chemisorbed on Lewis acid sites; surface silanols appear to make the gas-phase butene molecules accessible for proton exchange by reversible physisorption (*7*). Activated tungsten-oxide/silica resembles silica–alumina; on both catalysts silanol groups are found, and they contain Lewis acid sites of equal strength (*6*). It is conceivable, therefore, that the butene isomerizations on these catalysts proceed *via* identical mechanisms and on closely similar active centers. We will show that this concept can be used successfully to explain our experimental results.

In a previous paper (*6*) we concluded that the configuration of the tungsten surface compound on dehydrated tungsten-oxide/silica is predominantly **I** for WSI and WSR, and **II** for WSC (in these and the following drawings open-ended lines depict ≡Si—O bridges):


I

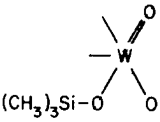

II

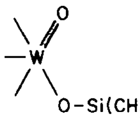
The observed Lewis acidity of WSC was ascribed to the coordinatively unsaturated nature of **II.** Thus, the interaction of alkene (e.g., propene) with the Lewis acid sites on activated tungsten-oxide/silica (e.g., WSC) can be written as


II **III** **IV** (7)

The ≡Si—O bridges to the silica lattice are electron-attracting groups, owing to the $p_\pi - d_\pi$ back-bonding between oxygen and silicon. Compound **II** has three such ligands, whereas **I** has only two. Obviously, **II** will be a stronger Lewis acid than **I,** so that alkenes chemisorbed on **II** should have a greater tendency to donate a proton. In accord with this prediction, the catalysts prepared by cogelation, WSC and WSCA, are more active in the double-bond isomerization of 2-butene than WSI and WSR.

Treating the tungsten-oxide/silica catalysts with hexamethyldisilazane converts the surface compounds **I** and **II** into **V** and **VI,** respectively (*6*):


V


VI

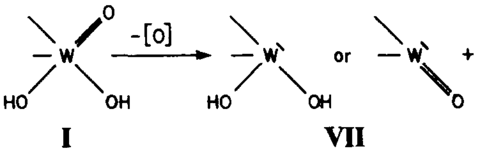
Owing to the increased number of ≡Si—O ligands, the Lewis acid strength of these two sites will be higher than that of the corresponding nontreated species, so that we expect an increased activity for isomerization. Silylation, however, also removes most of the surface silanols. The presence of such hydroxyls has been demonstrated to be necessary for the isomerization reaction to proceed (*7, 9*). On silylated tungsten-oxide/silica the increase of the isomerization activity due to the enhanced Lewis acidity probably competes with the activity decrease due to poisoning of the surface silanols. This results in the net activity increase for WSI and WSR, and the decrease for WSC and WSCA.

Ammonia treatment at temperatures around 700 K only marginally affects the isomerization activity of silica and silica–alumina (*7*). This agrees well with the present observations on tungsten-oxide/silica.

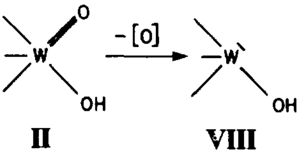
Metathesis

Figure 2 shows that silylation causes a 10- to 100-fold increase in the metathesis rate over our catalysts. Because the silylating compound, hexamethyldisilazane, poisons Brønsted-acidic surface hydroxyls, it is unlikely that these hydroxyls are involved in the formation of carbenes (Eq. (3)). The concept of a hydride intermediate (Eq. (2)) can, however, be retained by choosing another potential proton donor, viz., the Lewis acid–alkene complex mentioned in the foregoing section. This implies that the effect on the metathesis activity of changing the number of ≡Si—O ligands (by silylation or by going from WSR and WSI to WSC and WSCA) should be closely similar to the effects predicted for butene isomerization. This is indeed observed: WSC and WSCA are more active than WSR and WSI, and silylation greatly enhances the metathesis activity. In fact, structures **V** and **VI** are almost identical in terms of ≡Si—O ligands, which can explain why all catalysts have about the same metathesis activity after silylation (Fig. 2).

Usually, the metathesis activity of tungsten-oxide/silica increases on prolonged contact with propene. This transient behavior is known under the name of "catalyst break-in." The duration of the break-in can be greatly shortened by pretreating the catalyst with hydrogen or carbon monoxide (*14*) or by activating at temperatures above 900 K (*15*). This suggests that the break-in is a reduction step. The positive effect of ammonia on the metathesis activity might be explained from a partial reduction of the catalyst as well. The temporary nature of the ammonia-induced activity enhancement is possibly caused by the low number of activated sites, which makes the treated catalyst susceptible to poisoning by traces of oxygen or water. In terms of the proposed surface models for tungsten-oxide/silica (**I**, **II**), the break-in and the pretreatments can be depicted as:



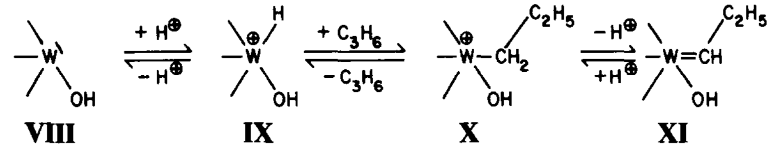
(8)



(9)

Tetravalent surface structures similar to **VII** and **VIII** have been suggested for the highly active catalyst systems derived from silica gel and π-methallyl tungsten compounds (*16*). The [O] in Eqs. (8) and (9) is probably evolved as water or carbon dioxide after reduction with hydrogen or carbon monoxide, as molecular oxygen after a high-temperature treatment, and as acetone (*17*) or its degradation products after contact with propene. In the systems described in this paper, catalyst break-in was not usually observed. Presumably, our treatment procedure causes a break-in faster than 1 min. The time scale of our experiments does not allow us to observe such a transient.

On the basis of the evidence now available we propose the following model for the initiation of propene metathesis on tungsten-oxide/silica, e.g., WSC:



(10)

Thus, a proton, originating from the Lewis acid–alkene complex **III** in Eq. (7), reacts with the Lewis base **VIII** to yield the tungsten hydride **IX**. Adsorption of propene on this hydride, followed by β-hydrogen addition, results in the formation of **X** (*5*). Back-donation of a proton to the tungsten complex **IV** in Eq. (7), finally, gives the carbenoid chain initiator **XI**. The reverse reaction of Eq. (10) is probably fast, resulting in a limited lifetime of the metal–carbene complex. This explains the observation that the metathesis on tungsten-oxide/silica can be temporarily suppressed without affecting the rate of isomerization by injecting a small amount of oxygen into the propene feed (*18*).

The interaction between tungsten and the silica surface appears to have a twofold function. Apart from enhancing the Lewis acid strength as already mentioned, the silica probably protects the surface compound from being reduced beyond the tetravalent state by shielding a large part of the tungsten coordination sphere.

Summarizing, the initiation of alkene metathesis on tungsten-oxide/silica can be described from the combined action of a Lewis acid–alkene complex serving as a proton donor–acceptor, and a tetravalent tungsten surface compound on which the actual carbene is formed. The promoting effect of Lewis acids and the formation of tetravalent transition-metal species, both from low- and high-valent precursors, are frequently observed in homogeneously catalyzed metathesis (see, e.g., Ref. (*19*)). Therefore, it might be possible that the generation of active centers in other metathesis systems, homogeneous as well as heterogeneous, can also be explained from a model such as that described here.

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