

Reduction Behavior and Metathesis Activity of $\text{WO}_3/\text{Al}_2\text{O}_3$ Catalysts

III. The Activation of $\text{WO}_3/\text{Al}_2\text{O}_3$ Catalysts

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The activation of $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts for the metathesis of propene (573 K, 0.1 MPa, flow reactor) was investigated. For catalysts containing ≤ 12 wt% WO_3 , the best activation procedure is a thermal treatment in flowing inert gas at a temperature depending on the WO_3 content (up to 1143 K at 0.5–4 wt% WO_3). The specific activity of W after these procedures and the reducibility of W(VI) show opposite trends. Hydrogen as an activation medium is inferior to Ar at WO_3 contents ≤ 12 wt% but with a 23-wt% $\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst conditions were found where activation in H_2 yields higher activities than an inert treatment at the same temperature. The propene metathesis was found to be first order in propene at 573 K and 0.1 MPa. The apparent activation energy decreases from 40 to 25 kJ/mole with increasing WO_3 content. The results imply that the active sites are formed exclusively from W(VI) precursors when the WO_3 content is ≤ 12 wt%. At high WO_3 content prerduction under appropriate conditions leads to surfaces with coexisting W(IV) and W(VI) precursors. © 1989 Academic Press, Inc.

INTRODUCTION

During the past 15 years much effort has been made to elucidate the nature of the active species of W- and Mo-based metathesis catalysts. During this time, a widely accepted answer has been found for the question of the active site structure, which is considered to be a metal carbene complex (1). On the other hand, extremely divergent conclusions have been drawn concerning the problem of which oxidation state of the metal is involved in the active sites or in their precursors. For supported MeO_3 (Me = Mo, W) catalysts, the oxidation states suggested are 0 (2), +2, +3 (3), +4 (4–8), +5 (9, 10), and +6 (11, 12). This resembles very much the situation described in the early papers of Hérisson and co-workers, who were the first to propose the carbene structure of the active site (1) but found in another investigation that some metathesis activity may be obtained starting from nearly all possible W oxida-

tion states, with superior performance, of course, of WOCl_4 (13).

From the literature cited above, the evidence supplied in favor of Me(IV) as an active site precursor appears to be most convincing. Several routes from Me(IV) precursors to the active metal carbene site have been proposed (7, 14, 15). On the other hand, the +6 state, which, on the basis of theoretical considerations (16), should be expected to form active metathesis sites as well, has been widely discarded from the discussion (exceptions: Mo(VI) as a site precursor inferior to Mo(IV) (11), Mo(VI) activated by UV irradiation (12)). This is due to the pronounced break-in phenomena observed in particular with SiO_2 -supported catalysts, which are reduced in the course of the nonstationary period. In line with this, a qualitative correlation between the reducibility of the oxidic component and its metathesis activity has been established (17, 18). This explains, for instance, the observed inferior performance

of WO_3 on Al_2O_3 compared to SiO_2 , with a difference of 1–2 orders of magnitude found at low WO_3 loadings (18, 19), as hexavalent tungsten is very difficult to reduce on Al_2O_3 (17, 20–22).

The work reported in this series was initiated by the successful activation of a catalyst (1 wt% $\text{WO}_3/\text{Al}_2\text{O}_3$ (23)), the reduction of which should require temperatures above 1200 K according to the literature (17). In part I (22), the extraordinary stability of W(VI) on Al_2O_3 confirmed by X-ray photoelectron spectroscopy was reported. It was concluded that intermediate W forms are not stable under the conditions required for the reduction of W(VI) in H_2 if the WO_3 loading is lower than 40% of a theoretical monolayer coverage of the support, while W(IV) may be present under certain reduction conditions if the WO_3 loading approaches (or exceeds) the monolayer capacity.

In part II (24), an EPR investigation of W(V) species, which are formed in quantities of <1% of the total tungsten content during typical thermal activation procedures and during the metathesis reaction itself, was presented. Two different W(V) species were discerned but both should be

considered by-products of the activation process or of the reaction. They do not exhibit any correlation with the metathesis activity.

The present paper (the last in the series) reports studies of the activation of $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts over a wide range of WO_3 loadings for the metathesis of propene. With consideration of the results of the previous parts, the response of the metathesis activity to the procedures applied (inert gas, H_2 , air, at pretreatment temperatures of 823–1193 K) serves to draw conclusions about the W oxidation states involved in the formation of the active sites.

EXPERIMENTAL

1. Materials. The catalysts were prepared by impregnation of $\gamma\text{-Al}_2\text{O}_3$ (VEB Leuna-Werke, GDR; BET surface ≈ 250 m^2/g , slightly varying due to different batches) with a solution of WO_3 in NH_4OH (pH = 8.8) by the incipient wetness technique. They were dried at 400 K, calcined in air at 823 K for 2 h and stored in air. Some characteristics of the catalysts are collected in Table I where nominal and actual WO_3 contents and BET areas after calcination at 823 K and after typical activa-

TABLE I
 WO_3 Contents and BET Areas of the Catalysts

Code	WO_3 content (wt%)		BET area (calcination at 823 K)		W loading ^b (atoms/nm ²)	BET area after activation at T_{act}^c	
	Nominal	Real ^a	(m ² /g)	(m ² /g Al_2O_3)		T_{act} (K)	(m ² /g)
W0.5	0.5	0.53	264	265	0.053	1143	167
W1	1.0	1.03	275	277	0.10	1143	162
W2	2.0	2.04	259	261	0.20	1143	142
W4	4.0	3.86	256	261	0.39	1143	146
W7 ^d	7.0	6.80	248	262	0.71	1093	189
W12	12.0	11.30	211	240	1.39	1023	181
W23 ^d	23.0	23.3	203	265	2.98	973	197

^a Determined by electron microprobe analysis.

^b Referred to BET area after calcination at 823 K.

^c After 2 h calcination in air at T_{act} (by analogy with activation procedures mentioned below, which are conducted in Ar).

^d Catalysts used in part I (22) of this series.

tion temperatures (*vide infra*) are given. The code used to denote the samples is illustrated in the table as well.

H₂, Ar, and propene from cylinders were deoxygenated over MnO/Al₂O₃, dried over Mg(ClO₄)₂, and repurified by an oxygen trap (MnO/Al₂O₃) at the reactor entrance. The propene (VEB PCK Schwedt/KB Böhlen) contained 0.07 vol% propane and 0.03 vol% ethene. The air for regeneration of the catalysts was dried over Zeosorb 4A molecular sieve (VEB CK Bitterfeld).

2. Reaction procedure. The metathesis of the undiluted propene was investigated in a flow reactor under atmospheric pressure and at 573 K if not stated otherwise. The catalysts were stable over many reaction-regeneration cycles. Typically, after completion of the regeneration (air, 823 K, 2 h), the catalyst (0.25–1 g, particle size 0.4–0.8 mm) was either cooled to the reaction temperature of 573 K (“activation in air at 823 K”) or, in general, heated in Ar to the activation temperature chosen. The activation was performed in flowing Ar or H₂ (6 liters/h, 2 h; an extension did not affect the results significantly). A combination of the activation medium and temperature (in K) will be used to denote the procedures applied, e.g., H₂, 973. After activation, the catalyst was cooled in Ar to 573 K and propene was charged. An induction period as reported for SiO₂-supported catalysts was not observed with our samples, where the effluent sampled after ≈5 min had the same composition as samples taken after 30 min time on stream, which was defined as the standard reaction period.

This procedure yielded reproducible activities except for an activation temperature of 823 K, where a sample history effect was found (low, poorly reproducible activities with fresh samples, high activity if the preceding run involved temperatures ≥1100 K). This effect was successfully avoided by a standardization of the sample history (fresh samples exposed to one reaction-regeneration cycle with Ar, 973) for this particular activation temperature.

The reaction products were analyzed by GC (10.5 m OPN/Porasil C packed column for C₁–C₄ hydrocarbons, 25 m OV-1 glass capillary column for C₅⁺, and C₁–C₄ as a sum). During the regeneration of the catalyst, the effluent air was directed through a NaOH trap to determine the burnt-off carbonaceous residue as CO₂.

The absence of pore and external diffusion limitations was checked by standard methods (0.2–0.4 and 0.6–0.8 mm particle sizes used for the pore limitation test). The influence of oxygen was demonstrated by introducing 30–40 ppm O₂ through the walls of a short piece of polyvinyl chloride tubing (oxygen content estimated from the progression of the dark zone in a MnO/Al₂O₃ bed). The metathesis activity was reduced by this by an order of magnitude.

In preliminary series performed with gases of 1–2 ppm residual oxygen content (without an oxygen trap at the reactor entrance, cited below as “preliminary runs”) activities were found to be 30–60% of those reported below but the same tendencies and regularities were observed. This parallelism of the activities at two different levels of feed purity may serve as additional evidence that the results presented below are not influenced by an interchange between the kinetic and the diffusional reaction regimes.

3. Data presentation. At conversions of $x = 0.1$ – 0.35 , i.e., not too close to the equilibrium conversion of $x_{\infty} \approx 0.45$ (estimated for 573 K from (25) and (26)), products other than C₂–C₄ olefines amounted to 0.1–1% of the total hydrocarbons. These products (propane, C₅-, C₆-, and C₇-hydrocarbons) will be neglected therefore. The butene–ethene ratio averaged over more than 40 runs was 1.06 ± 0.08 . Only at conversions above 0.4 was an increase of C₄ products at the expense of ethene noted. The butene isomerization was at equilibrium (butene-(1): *cis*-butene-(2): *trans*-butene-(2) = 0.30:0.65:1 (exp.); theoretical ratio 0.29:0.65:1 (25, 26)) except for a decreased butene-(1) fraction at very high

feed rates. Coke formation corresponded to propene conversions of less than 0.001 and will also not be discussed.

In the following, activities will be reported as formal turnover numbers T_N , i.e., initial rates of propene conversion referred to the total WO_3 amount of the sample. Although it would have been possible to derive initial rates for most of the series without any assumption, we made use of the kinetic rate law observed with the fully activated samples (first order reversible reaction, see Kinetic Aspects) for the extrapolation to differential conversions.

The last column of Table I gives an estimate of the loss of internal support surface area during the activation procedures employed (treatments at typical activation temperatures performed in a muffle furnace prior to BET measurements). However, it has been shown recently that the tungsten remains segregated after the thermal degradation of the pore system at even higher temperatures (27) and should be fully accessible to gas molecules. Our activity data are, therefore, presented without any regard to the surface area loss.

RESULTS

1. Activation in a Nonreductive Atmosphere

$\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts may be activated for the metathesis reaction by a thermal treatment in a flowing inert gas, e.g., Ar. It has been mentioned earlier that the activity rises with increasing activation temperature T_a (up to 970 K applied to a 6% $\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst (19)). We found (Fig. 1) that the metathesis activity levels off at activation temperatures specific to each catalyst and remains constant when T_a is raised further by 50–100 K. The temperatures necessary to attain the constant activity level increase drastically with decreasing WO_3 content.

In Fig. 2, it can be seen that the specific activity increases with decreasing WO_3 content down to the 0.5- to 1-wt% region provided that the appropriate activation

temperatures are applied (curve 1). These temperatures are as high as 1143 K at WO_3 contents below 4 wt% but do not increase further as has been verified by single runs with $T_a = 1193$ K for each catalyst in this region. The specific activities of tungsten obtained with $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts as shown in Fig. 2 are quite comparable to the activities reported for WO_3/SiO_2 (28), in particular at low tungsten loadings. On the other hand, if T_a is kept at a constant (lower) level for the whole range of WO_3 contents the catalysts with low WO_3 loading will appear to be inactive. This picture, which was reported in (17), is illustrated by curves 2 ($T_a = 973$ K) and 3 ($T_a = 823$ K).

Figure 2 also contains some activity data obtained after activation in air at 823 K. The activity is generally somewhat lower than after Ar, 823. An attempt to activate the W12 catalyst with moist air ($p_{\text{H}_2\text{O}} \approx 2.6$ kPa) failed. The activity was almost completely suppressed, but it was fully reversed when an Ar treatment (973 K) was applied.

2. Influence of Hydrogen

Marked differences in the response of the metathesis activity to H_2 pretreatments were found between W23 (≈ 3 W atoms/ nm^2), the sample with the maximum WO_3 content, and the remaining catalysts (≤ 1.5 W atoms/ nm^2). Figure 3 shows the influence of H_2 treatments on the metathesis activity of W12. It is obvious that the turnover numbers measured after H_2 treatments (curve 2) are inferior to those resulting from the inert gas procedure, which are repeated in curve 1 for comparison, for the whole range of activation temperatures. When samples activated in H_2 were subsequently purged with Ar for 2 h at the same temperature, their activity increased markedly as indicated by arrows in the figure. For $T_a \leq 973$ K, the influence of H_2 was completely reversed and the catalyst behaved as if activated merely in Ar. For $T_a > 973$ K, the

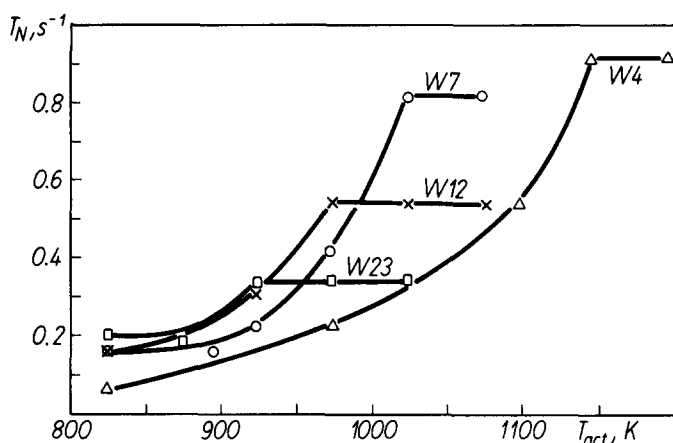


FIG. 1. Thermal activation of $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts: dependence of the metathesis activity on the activation temperature. Activation medium, Ar; length of activation period, 2 h.

detrimental effect of H_2 partially persisted after the Ar purge (curve 3).

The most important of these trends were again observed with W7. At $T_a = 823$ K, no significant difference was found between the activating effect of Ar and H_2 but at 973

K the activity after the H_2 treatment was only about 50% of that after the Ar treatment. Again, the loss of activity was reversed by an additional 2-h Ar purge.

For W7 and W4 it was attempted to enhance the activity of the Ar-treated samples

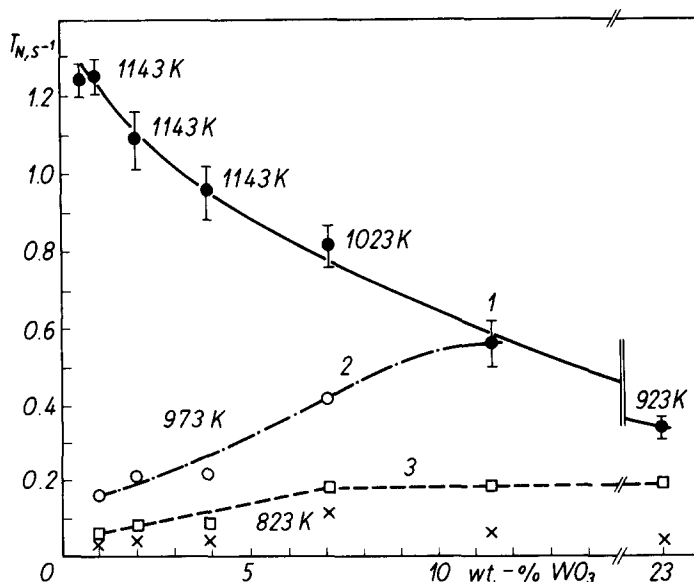


FIG. 2. Thermal activation of $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts. Dependence of the metathesis activity on the WO_3 content. Curves: (1) (●) Fully activated samples; activation temperatures inserted in the diagram; vertical bars indicate standard deviation. (2) (○) Activation at 973 K. (3) (□) Activation at 823 K. (×) Activation in air at 823 K.

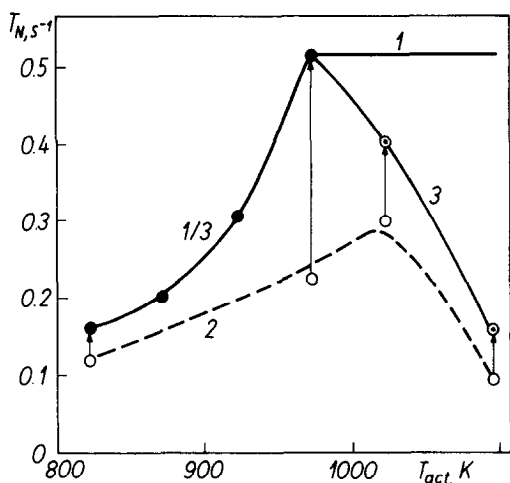


FIG. 3. The effect of hydrogen in the activation of a 11.3-wt% $\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst. Length of activation period, 2 h. Activation medium: (●) Ar (curve 1), (○) H_2 (curve 2), (⊙) H_2 , with additional 2-h Ar treatment (curve 3 partially identical with curve 1; the arrows indicate the effect of the Ar treatment).

(1073 and 1143 K, resp.) by short-time reduction under more severe conditions.¹ However, only activity losses were observed after 15 min reduction at 1093 K (21 and 11%, resp., related to activity after Ar treatment) and 1143 K (33 and 24%, resp.).

A low-temperature hydrogen treatment (W12; H_2 , 623) of a surface previously regenerated in air (i.e., air, 823) resulted in a drastic activity drop ($T_N \approx 0.01 \text{ s}^{-1}$ compared to 0.08 s^{-1} after air, 823). In contrast, a H_2 , 623 treatment of samples previously activated in Ar at 1073 K caused activity losses of only 15–20%.

The influence of H_2 on the metathesis activity of W23 is illustrated in Fig. 4a in a representation analogous to Fig. 3. The behavior of W23 contrasts to that of the catalysts with lower WO_3 content in the 923- to 973-K region where the H_2 treatment results in a higher activity than the activation in Ar. This advantage gets lost when the pretreatment temperature is raised to 1023 K. A similar development of the

metathesis activity may be observed with W23 when the length of the pretreatment is varied at 973 K (Fig. 4b, curve 2). The conversion passes through a distinct maximum, which in the extrapolation to differential conversion would yield a T_N of nearly 0.7 s^{-1} . Obviously, the value given in Fig. 4a, which was obtained after 2 h of reduction, represents a sample that has been considerably "overreduced." At a reduction temperature of 923 K (curve 1), the propene conversion increases smoothly and converges toward the value included in Fig. 4a.

3. Kinetic Aspects

The kinetic reaction order of propene was determined with W1, W4, and W12 for the fully activated state (see legend of Fig. 5) by diluting the propene with Ar up to a ratio of 1:10. For W4 and W12 two different feed velocities were selected in order to obtain conversions near 0.1 and above 0.2. In all cases the conversion proved to be independent of the initial propene concentration, which indicates a reaction order of 1 for propene. In Fig. 5a, this is confirmed by a logarithmic plot of the reaction rate versus the initial propene concentration c_P^0 . The linear relation at conversions far from differential is obtained only if both propene metathesis and reverse reaction are first order, i.e., $x \neq f(c_P^0)$ (see Eqs. (1) and (2)). Hence, the kinetic rate law has the form

$$r = c_P^0 \frac{dx}{dt} = k_1 c_P - \frac{1}{2} k_{-1} (c_P^0 - c_P) \quad (1)$$

$$= c_P^0 (k_1 (1 - x) - k'_{-1} x), \quad (2)$$

where k_1 and k_{-1} are the rate constants of the propene metathesis and the reverse reaction, $k'_{-1} = k_{-1}/2$, and c_P is the propene concentration at the time t . The conventional mathematical formalism yields

$$\ln \frac{x_\infty}{x_\infty - x} = (k_1 + k'_{-1}) t, \text{ and} \quad (3)$$

$$k_1 = (k_1 + k'_{-1}) x_\infty. \quad (4)$$

The same kinetics were found for the "preliminary" level of feed purity.

¹ Preliminary runs (see Experimental).

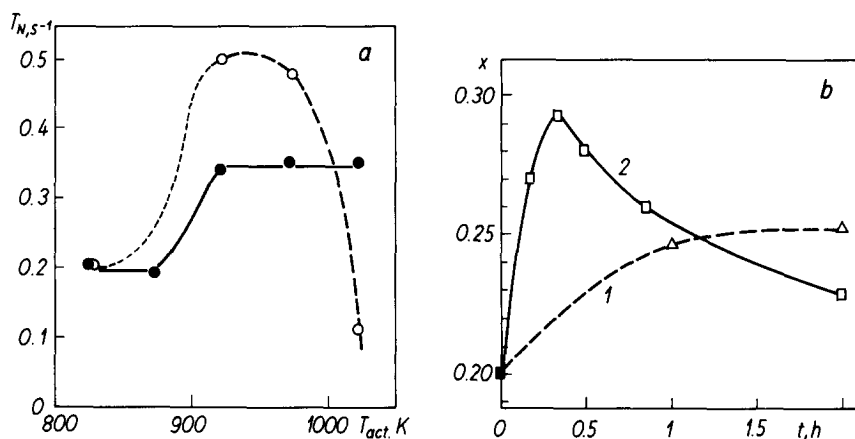


FIG. 4. The effect of hydrogen in the activation of a 23.3-wt% WO₃/Al₂O₃ catalyst. (a) Variation in the activation temperature; length of activation period, 2 h; activation medium: (●) Ar, (○) H₂. (b) Variation in the length of the activation period; activation medium, H₂; activation temperature: (Δ) 923 K (curve 1), (□) 973 K (curve 2). $t = 0$ corresponds to a 2-h activation in Ar at 923 or 973 K.

Figure 5b illustrates for some examples that Eq. (3), indeed, holds up to relatively high conversions. The choice of the equilibrium conversion, x_{∞} , is not very critical for the evaluation of k_1 if the conversions are not too close to the equilibrium level. For our data at 573 K, an increase of x_{∞} from 0.45 to 0.5 would cause a decrease in the k_1

values by 3–4%_{rel}. The more relevant metathesis rate constants measured in this study are tabulated in Table 2.

The stability of the metathesis activities was tested by extending the reaction period to 3 h. No deactivation was observed in this time for all catalysts except W23. After 180 min the activity of the latter (expressed as

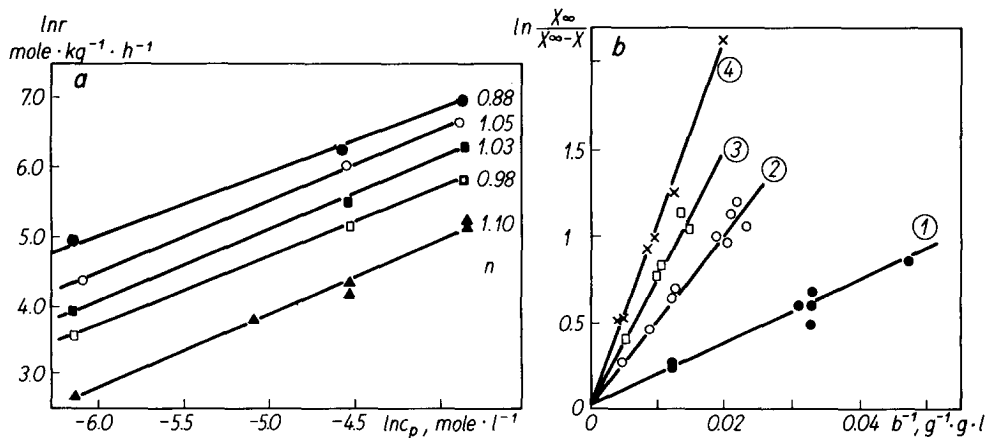


FIG. 5. Kinetics of the propene metathesis over WO₃/Al₂O₃ at 573 K and 0.1 MPa. (a) Determination of the reaction order n of propene: (●) W12, 2 h Ar, 973 K, $b \approx 500 \text{ g} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, $x \approx 0.10$; (○) W12, 2 h Ar, 973 K, $b \approx 125 \text{ g} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, $x \approx 0.25$; (■) W4, 2 h Ar, 1143 K, $b \approx 225 \text{ g} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, $x \approx 0.10$; (□) W4, 2 h Ar, 1143 K, $b \approx 45 \text{ g} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, $x \approx 0.30$; (▲) W1, 2 h Ar, 1143 K, $b \approx 77 \text{ g} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, $x \approx 0.10$. The reaction orders found are inserted in the diagram. (b) Reversible first-order kinetics of the propene metathesis; $x_{\infty} = 0.45$. Curves: (1) W1, 2 h Ar, 1143 K (●); (2) W4, 2 h Ar, 1143 K (○); (3) W7, 2 h Ar, 1023 K (□); (4) W23, 2 h Ar, 923 K (×).

TABLE 2

Metathesis Rate Constants (According to Eqs. (3) and (4)) and Apparent Activation Energies for $\text{WO}_3/\text{Al}_2\text{O}_3$ Catalysts after Thermal Activation in Ar

Sample	T_{act} (K)	$10^3 k_1$ ($\text{m}^3 \cdot \text{kg}^{-1} \cdot \text{h}^{-1}$) at 573 K	E_a (kJ/mole) for 523–623 K
W0.5	1143	1.33	41.5
W1	1143	2.62	35.8
W2	1143	4.69	32.4
W4	1143	7.49	25.8
W7	1023	11.29	26.6
W12	973	14.33	22.5
W23	923	15.67	—

k_1) decreased to $\approx 75\%$ of the 30-min level with samples activated in Ar or by a 20-min H_2 reduction at 973 K, and to $\approx 60\%$ with a sample pretreated merely in air. With a feed less rigorously purified of oxygen ("preliminary runs," 1–2 ppm O_2) considerable deactivation was found with all catalysts. For example, after 60 min, the activity found with W12 had decreased to $\approx 80\%$ of the 30-min level with a sample activated in Ar and to $\approx 60\%$ with an air-treated sample.

Figure 6 presents some data on the temperature dependence of the propene metathesis over fully activated $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts. The runs were performed in a manner proposed by Andreini and Mol (19, 28), i.e., at a constant feed rate, a series of

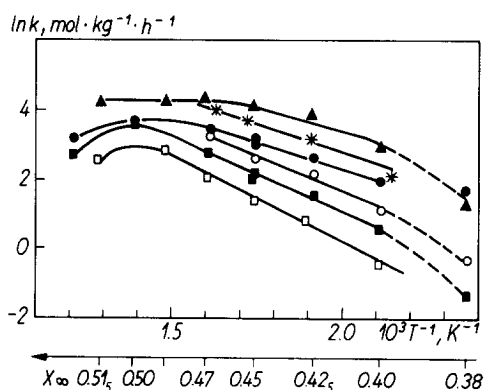


FIG. 6. Temperature dependence of the propene metathesis over $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts. (\square) W0.5, (\blacksquare) W1, (\circ) W2, (\bullet) W4, ($*$) W7, (\blacktriangle) W12 (\blacktriangle raised by 0.5 units for the sake of clarity). x_∞ , equilibrium conversion used for the evaluation of k_1 (25, 26).

reaction product samples was withdrawn while the catalyst underwent heating and cooling according to a specified program, with a 15-min isothermal period at every reaction temperature selected. In our experiments the temperature sequence was (in K): 573, 473, 373, 423, 523, 623, higher temperatures. The equilibrium conversions x_∞ used for the evaluation of k_1 are inserted in the diagram. The extensive extrapolation involved in their estimation on the basis of data from (25, 26) appears to be permissible in view of the above-mentioned insensitivity of k_1 to x_∞ . Of course, the method implies the assumption that the kinetics do not change in the temperature range considered. It should be noted, however, that the propene conversions observed exhibited the same tendencies as the rate constants evaluated from them.

As anticipated by Andreini and Mol (19, 28) the temperature dependence of the metathesis rate constant is complex. The $\ln k_1$ vs T^{-1} relationship appears to be nonlinear, with a maximum in the 673- to 723-K temperature range, which is very broad for the catalysts containing higher amounts of tungsten. In the 523- to 623-K range linear sections are found in particular at low WO_3 content but below 473 K the rate constants fall below the values predicted by the straight lines shown in the diagram. The (apparent) activation energies for the 523- to 623-K temperature range depend on the WO_3 content, varying from 41 to 22 kJ/mole (Table 2). The values of x_∞ used in the calculations (see Fig. 6) imply that the apparent activation energy of the reverse reaction is lower by 4–5 kJ/mole than that of the propene metathesis (cf. Eq. (4)).

During the experiments no hysteresis phenomena were found upon cooling and reheating the catalyst as long as the activity maximum was not exceeded. The temperature variation also had some influence on the product composition. Thus, butene-(1), which was at equilibrium at 573 K, was almost absent below 523 K. At $T \geq 623$ K the ethene yield exceeded the butene yield by

15–35%_{rel}, which is considerably more than covered by the amount of the consecutive products (pentenes).

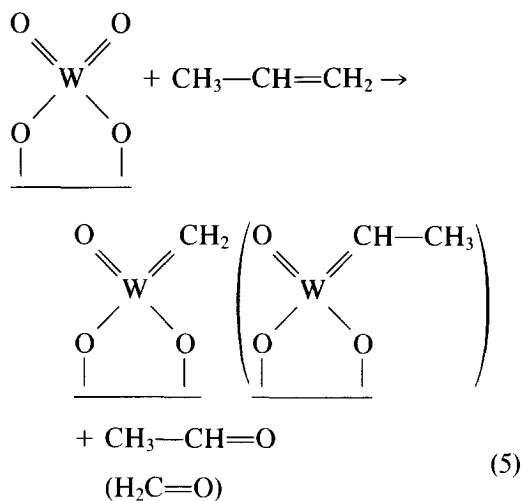
DISCUSSION

The XPS and EPR investigations reported in the previous parts of this series (22, 24) showed that W(VI), W(V), W(IV), and W(0) are the states in which tungsten may be present after the activation procedures used in this study. The vast majority of the tungsten species is in the +6 state. W metal is the reduction product formed under the severe conditions necessary to reduce the alumina supported W(VI) to an appreciable extent. The presence of W(IV) is limited to catalysts with high WO₃ loading (W23), which are reduced under less severe conditions (22). W(V) is formed to a small extent during all reductive and thermal treatments at temperatures down to 573 K (e.g., during the metathesis reaction as well) but it has been proven to be irrelevant to metathesis (24). It has been shown in the literature (17, 20, 21) as well as in the preceding parts of this paper that the reducibility of W(VI)/Al₂O₃ decreases with decreasing WO₃ content. This applies to the reduction to metallic tungsten (20–22) as well as to W(IV) (22) and to W(V) (24).

On this basis it may be concluded from the results presented above that the tungsten carbene entities considered as the active sites of metathesis can be formed starting from W(VI) species without their previous reduction to W(IV) and that W(VI) is the only active site precursor on WO₃/Al₂O₃ catalysts with WO₃ loadings far from the theoretical monolayer capacity of the Al₂O₃. Support to this conclusion is not so much supplied by the predominance of W(VI) on the surface, which would be open to objections on the basis of the view that only a small fraction of the active component is involved in the catalytic sites of metathesis; rather, the decisive arguments are the inverse tendencies of the reducibility and the metathesis activity with varying WO₃ content and the inability of H₂ to im-

prove the performance of the catalysts if the WO₃ content is ≤ 12 wt%. The observation that the influence of H₂ on the metathesis activity of W12 (and W7), which is negative anyway, may be completely reversed by Ar treatments (Fig. 3, for $T_a \leq 973$ K) also implies that it is not a reduction product possibly formed but the remaining form, W(VI), that is relevant to metathesis.

A reaction pathway for the formation of carbene sites from hexavalent species was proposed by Rappé and Goddard (16). Future work will show if it supplies an actual route for carbene formation on the surface of thermally activated WO₃/Al₂O₃ catalysts, e.g.:



The reduction which accompanies the carbene formation in Eq. (5) seems to be in contradiction to the high stabilization exerted on the W(VI) state by the Al₂O₃ support. However, the carbene formation is essentially a ligand exchange that does not affect the bonds to the surface. It has been shown in other cases (sulfidation in H₂/H₂S, hydrochlorination of MoO₃/Al₂O₃ and WO₃/Al₂O₃ surfaces) that reductions accompanied by ligand exchange processes may proceed at temperatures much lower than those of beginning H₂ reduction (24, 29, 30). In the MoO₃/Al₂O₃ system, the latter has been shown by Segawa and Hall (31) to break the Mo–O–Al bond, and it may be

a high stabilization of the W–O–Al bond that is the reason for the low affinity of W(VI)/Al₂O₃ to reduction by H₂.

In the case of W23 the activity may be considered as a sum of a basic contribution, which is induced by the thermal treatment at $T = 923$ K and should be due to W(VI) precursors, and an "excess activity," which depends on the reduction state of the catalyst and is due to a tungsten state intermediate between W(VI) and W(0) (see Fig. 4). As the temperature region where this "excess activity" comes into play fits well the conditions under which W(IV) was observed by XPS (22) we conclude that it is W(IV) that forms the additional active sites. This is in line with earlier results of Startsev *et al.* (4) for silica supported organotungsten-derived systems and with a large body of evidence accumulated in the literature for Mo-based heterogeneous metathesis catalysts (6–8). Several reaction pathways for the formation of surface carbenes from tetravalent precursors were proposed in the literature (7, 14, 15) and were discussed in detail in (7).

In the activation with H₂, an activity drop (compared to the activation in an inert medium) that can no longer be reversed by simple thermal treatments occurs when the activation temperature exceeds critical values, which depend on the WO₃ content (Figs. 3 and 4a). We ascribe this to the formation of W metal as observed by XPS (22). Hence, W(0) proves to be practically inactive in the metathesis reaction.

The activation of the W(VI) precursors must be explained by thermal, most likely by desorption, processes. We assume that coordinatively unsaturated sites are created at sites previously blocked by adsorbed molecules (O₂, H₂O, H₂) or interacting neighboring surface groups (OH). The material presented here furnishes several examples of the favorable influence of the desorption of these species. Thus, the reversal of the relative activity losses in H₂ treatments by Ar purges (Fig. 3) without significant changes in the W oxidation state

(22, 24) suggests that hydrogen may be adsorbed on the WO₃/Al₂O₃ surface at temperatures as high as 973 K and must be desorbed. The presence of relatively weakly bound oxygen on the surface after air, 823, is indicated by the activating effect of Ar, 823, compared to air, 823 (Fig. 2), but also by the different effect of H₂, 623, on surfaces after air, 823, and after Ar, 1073 (see Influence of Hydrogen). The difference cannot be explained by hydrogen adsorption but must be due to an interaction of H₂ with a species which is no longer present after Ar, 1073. Most probably, this is adsorbed oxygen, which would form the effective poison H₂O on H₂, 623. The poisoning action of OH groups is documented in our study by the comparison between two runs in which W12 samples were activated in dry and in moist air at 823 K. While the activity of the former sample was only slightly lower than that of an Ar-treated catalyst (cf. Fig. 2), the latter, the hydroxylation degree of which should be considerably higher, was completely inactive. The sample history influence on fresh catalysts activated at 823 K (see Experimental) should also be due to OH groups, which are not reproducibly removed at this temperature.

Nevertheless, the high temperatures necessary to activate catalysts concerning ≤ 4 wt% WO₃ require a further explanation. From data in the literature it may be concluded that the OH group density on the Al₂O₃ surface falls to 10–20% of the monolayer density at a dehydroxylation temperature as low as 873 K (32). It would be hard to rationalize how these OH groups could seriously interfere with tungstate entities present in a quantity of 2–12% of the monolayer density. Hence, we assume that OH groups adjacent to tungstate species are stabilized by the interaction with the sites that they are blocking. The desorption of these OH groups would require much higher temperatures than the breakdown of the surrounding OH layer. On the other hand, the removal of these stabilized OH

groups might be facilitated when they become neighbors themselves, which should occur with increasing probability at higher WO_3 loadings and would explain the lower temperatures required for the activation of these catalysts.

The activity obtained from W(VI) precursors by thermal activation procedures exhibits a high stability. During 180 min time on stream no decline was detected except for the case of W23; the samples maintained their white color during this time and the quantity of retained carbon was at the detection limit of the analytical method employed. We assume that coke formation plays a minor role with catalysts containing ≤ 12 wt% WO_3 (≤ 1.5 W atoms/nm²), any deactivation observed being due to poisoning by oxygen (e.g., in the feed as in the "preliminary runs" or on the surface in the case of air-pretreated samples). Coke formation may become involved in the case of W23, which was black after 180 min time on stream, with an unstable activity found irrespective of the activation procedure.

In the literature, a variety of kinetic models has been used to describe the kinetics of the propene metathesis over conventional impregnation ((33) and references cited therein (34)) and carbonyl derived catalysts (35). The complex rate laws obtained were considered to reflect the rate-determining role of the surface reaction. A reaction order of 1 as found in our study may indicate that an adsorption or desorption (e.g., the adsorption of the olefine molecule onto the carbene site) is the rate-determining step (rds). The same reaction order can be obtained when the reaction of an adsorbed propene molecule with a carbene site is rate determining. Here, the order reflects the exponent of the Freundlich-type isotherm (7), and an exponent of 1 would be required to explain the results. The temperature dependence of the rate constants (Fig. 6) may indicate that a change in the rds could have occurred below 473 K. The apparent activation energies given in Table 2 must, of course, be discussed with some

caution as their evaluation is based on several assumptions (see Kinetic Aspects). Nevertheless, the increase in the activation energy with decreasing WO_3 content appears to be well established. Apparent activation energies given in the literature for WO_3/SiO_2 (36) and for Mo-based catalysts ((33) and references cited therein (34, 35)) vary over the region of 23–35 kJ/mole.

For any discussion of the active site structure, the coordination properties of surface tungstate (and molybdate) species must be considered. After several years of controversy concerning the octahedral or tetrahedral coordination of the metal ions (37–39) recent XANES investigations of $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts (40) suggest that at low WO_3 content the tungsten is present as isolated tetrahedral surface tungstate species. Certainly, species of this structure type (not necessarily all of them) may be considered to be the W(VI) active site precursors at low WO_3 content.

Considerable activity (and lower apparent activation energy) has also been obtained with samples containing high amounts of WO_3 (e.g., W12, $\approx 35\%$ of the monolayer coverage). According to (40) their surface may be considered to be covered by bridged tetrahedral and octahedral surface tungstate structures. Hence, it may be suggested that other structures, e.g., bridged tetrahedra, may be potential precursors as well, but unequivocal evidence for this proposal is not available. It is tempting to assume that the shift in the apparent activation energy, which is probably related to the varying strength of the interaction with the surface (by analogy with the relation between reducibility and surface interaction (20–22)) reflects a modification of the active site structure. However, this shift, which is already observed at very low loadings, may equally well be due to a variation in ligand strength, i.e., the surface interaction of the isolated tetrahedral sites, the decreasing abundance of which would explain the lower turnover numbers.

The high "excess activity" observed af-

ter the reduction of W23 under certain conditions (cf. Fig. 4) gives rise to the idea that the sites derived from W(IV) may have a structure different from that of the W(VI)-derived sites. The activity of W23 is enhanced about twofold by a W(IV) quantity, which according to the results of part I of this series (22) should not exceed 10% of the tungsten present. A turnover number of $3\text{--}4\text{ s}^{-1}$ for W(IV)-derived sites may be estimated from these data. This is much higher than any value found for W(VI)-derived sites although it must be kept in mind that in both cases the actual number of active sites is not known. However, it has been pointed out that the tetrahedral tungstate sites are most difficult to reduce by H_2 (20, 22, 24, 40) and that the occurrence of W(IV) in the reduction of catalysts with WO_3 loadings near the monolayer coverage should be due to the octahedral structures, which are reduced under relatively mild conditions (973 K (22)). If the correlation drawn by us between the occurrence of the "excess activity" and the presence of tetravalent tungsten on the surface of W23 holds, the metathesis site derived from the W(IV) species must have been formed from an octahedral entity. More work is, however, necessary to substantiate this view.

CONCLUSIONS

$\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts have been activated for the metathesis of propene by thermal treatment in a flowing inert gas. The activation temperatures depend on the WO_3 loading ranging from 923 K for 3 W atoms/ nm^2 to 1143 K for 0.4 W atoms/ nm^2 . The specific activity of W on the fully activated catalysts increases with decreasing WO_3 content and hence shows a trend opposite to the reducibility of W(VI).

H_2 as an activation medium has been inferior to inert gas or has yielded at most identical activities for catalysts with ≤ 1.5 W atoms/ nm^2 . For catalysts with ≈ 3 W atoms/ nm^2 , conditions have been found where activation in H_2 yields higher activi-

ties than an inert treatment at the same temperature.

The propene metathesis over $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts is first order in propene at 573 K and 0.1 MPa. The apparent activation energy depends on the WO_3 loading, decreasing from ≈ 40 kJ/mole at 0.5 W atoms/ nm^2 to ≈ 22 kJ/mole at 0.4 W atoms/ nm^2 . Neither induction periods nor deactivation phenomena have been found with catalysts containing ≤ 1.5 W atoms/ nm^2 .

On surfaces with ≤ 1.5 W atoms/ nm^2 the active sites are formed from W(VI) precursors, which are most probably isolated tetrahedral surface tungstate species at very low WO_3 loadings. Additional active sites may arise from W(IV) precursors, which are formed in the partial reduction of catalysts with high tungsten content (≈ 3 W atoms/ nm^2).

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