

Reduction Behavior and Metathesis Activity of WO_3/Al_2O_3 Catalysts

II. The Role of W(V)—An EPR Investigation

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WO_3/Al_2O_3 catalysts of varying WO_3 contents (4–10 wt%) were subjected to various thermal and reductive treatments, used in the metathesis of propene (573 K, 0.1 MPa), and investigated by EPR spectroscopy. Three characteristic EPR signals were obtained, two of which were assigned to W(V) in different distorted octahedral sites. The third was due to a Mo trace impurity. Tetrahedral sites expected to be predominant on the surface were not detected by EPR probably due to their low reducibility. It was found that Mo impurities may affect the EPR spectra of such systems considerably. By evaluation of spin concentrations it was shown that less than 1% of the tungsten present was reduced to W(V). This percentage was increased by a treatment with dry HCl at 295 K, which was accompanied by a simplification of the spectrum, but it was concluded that the HCl treatment does not unambiguously prove the presence of W(V) paired structures in this system. By analysis of spin concentrations and metathesis activities it was demonstrated that W(V) is not relevant to the metathesis reaction but should be considered a by-product of the activation processes, which probably involve W(VI) as an active site precursor. © 1989 Academic Press, Inc.

INTRODUCTION

The catalytic and physicochemical properties of tungsta- and molybdena-based metathesis catalysts have been the subject of numerous investigations in recent years. It has been widely accepted that the active site (or its precursor) should contain the metal in a high oxidation state (1–10). Most authors, however, exclude the hexavalent state as a possible active site precursor due to pronounced break-in phenomena observed in metathesis experiments, in particular with silica-supported systems (11, 12) and in view of correlations between the reducibility of the catalysts and their metathesis activity (8, 13).

In our recent work we have found that WO_3/Al_2O_3 catalysts can be effectively activated for the metathesis of propene by a simple thermal treatment in an inert gas flow (14). This may be considered to indicate the catalytic significance of W(VI) species, the more so as XPS investigations

show that hexavalent tungsten on an alumina support is reduced in hydrogen only under drastic conditions and (except for catalysts with high WO_3 content where W(IV) can be detected (15), transforms directly to W(0) (15–17). On the other hand, the possibility that the catalysts are reduced to a small extent during the thermal treatment or the metathesis reaction cannot be excluded. Several authors ascribe the catalytic activity to pentavalent W (or Mo) (2, 3), and the assumption that only a small fraction of the metal ions present is involved in the metathesis reaction is quite common in the literature (1, 18–20). Unfortunately, the XPS signals of W(VI) and W(V) interfere considerably, and a significant quantity of W(V) may have escaped unobserved (15).

The EPR investigation presented in this paper was performed to solve the problem of the presence and the catalytic significance of W(V)/ Al_2O_3 in the catalyst state active for metathesis. Unlike the $MoO_3/$

Al₂O₃ system, which has been studied in great detail (21–23), the WO₃/Al₂O₃ system has not yet attracted much attention. W(V) signals of impregnated and of tungsten carbonyl-derived samples have been described in (24). Further data relevant to our work have been reported in studies of supported heteropoly acids (25) and of unsupported tungsten compounds (25–29).

EXPERIMENTAL

Materials. Catalysts of 4, 7, and 10 wt% WO₃ on alumina were obtained by repeated impregnation of “pural” alumina (Condea, 240 m²/g) with a solution of (NH₄)₁₀W₁₂O₄₁ (Reachim, Moscow; pH of solution >8; 40 g WO₃ per liter). The catalysts were dried at 400 K and calcined in air at 823 K for 2 h prior to use. Their actual WO₃ contents as determined by electron microprobe analysis were 3.8, 6.7, and 10.3 wt%, and they will be referred to as W4, W7, and W10, respectively.

The molybdenum content of the W10 sample was determined by optical spectral analysis (PGS 2 spectrograph, VEB Carl Zeiss Jena). As it proved to be near the limit of detection the result (20–30 ppm Mo/Al₂O₃) should be considered an estimate. This molybdenum originates predominantly from the support but it is not known in which form (bulk, bound to the surface, physically admixed) it is present. An additional sample (12 wt% WO₃) was prepared from a Mo-containing solution of WO₃ in NH₄OH. Its Mo content was found to be 590 ppm.

The Ar and H₂ used in sample preparation were deoxygenated over MnO/Al₂O₃ and dried over Mg(ClO₄)₂. The propene (VEB PCK Schwedt, KB Böhlen) contained 0.07 wt% propane and 0.03 wt% ethene. It was deoxygenated over MnO/Al₂O₃. The HCl gas (Matheson Ltd.) was used without further purification.

EPR sample preparation. Samples were prepared in a quartz flow reactor equipped with a side arm connected with a sealable EPR sample tube (quartz tube with glass

section). The samples were oxidized in a muffle furnace (2 h, 823 K) prior to the experiments. In runs with omission of the activation procedure the oxidation was repeated in the reactor with dried or moist (≈2.5 vol% H₂O) air.

Short beds of MnO/Al₂O₃ and Zeosorb molecular sieve (VEB CK Bitterfeld) at the reactor entrance, which were activated at the beginning of each run, served to trap residual oxygen and water traces, respectively. After evacuation and refilling of the system with Ar the catalyst sample was subjected to an activation procedure (thermal treatment in Ar, reduction in H₂, gas flow rate 6 liters/h, *T* = 973–1143 K) and cooled in Ar to 573 K. At this temperature, propene was charged at atmospheric pressure for 30 min and the reaction product was sampled for GC analysis. Finally, the furnace was removed, part of the catalyst was transferred to the EPR tube in an Ar flow by tilting the reactor by an appropriate angle, and the EPR tube was sealed off. In some cases, the catalyst sample was treated with a flow of dry HCl gas (≈10 liters/h, 15 min, in general at room temperature) after the metathesis run.

The reaction product was analyzed by GC (10.5 m OPN/Porasil C packed column for C₂–C₄ products, C₃⁺ being negligible at conversions <10%). The selectivity for metathesis products was >99.8%, the ratio of C₄ to C₂ olefins was ~1. The activities are reported as initial rates of propene consumption referred to the quantity of W in the catalyst (moles propene · s⁻¹ · moles W⁻¹), which may be considered a turnover number *T_N* (s⁻¹). Despite some drawbacks of the EPR sample preparation system with respect to kinetic work the activities measured correspond fairly well to data obtained in a conventional flow reactor system in a more detailed study of the metathesis activity of WO₃/Al₂O₃ catalysts, which will be published in part III of this series (30). The activities are less by 30–40%, which may be due to ill-defined temperatures in the catalyst bed during the reaction

as small quantities of catalysts (0.15–0.20 g) were charged with high propene flows (~60 liters/h) without any preheating section.

EPR measurements. EPR measurements were performed at 123 and 298 K with an ERS 220 spectrometer (Scientific Equipment Center, GDR Academy of Sciences) operating in the X-band and equipped with 100 kHz field modulation. The content of W(V) was measured at 298 K and evaluated using a computer program allowing base-line adjustments and comparison with a reference (ultramarine).

RESULTS

In the oxidized state, the catalysts did not exhibit any EPR signal. Figures 1–3 show EPR spectra recorded after various thermal, reductive, and HCl treatments of the catalyst samples. Table I summarizes the signal intensities and the metathesis activities. It can be seen that the reduction extent was generally low. The limitation of the intensity evaluation to certain signals is discussed in the following section.

Thermal and reductive treatments. With the W10 catalysts, a thermal treatment sufficient to bring about their full metathesis activity (Ar, 1073 K, 2 h) gave rise to spectrum A shown in Fig. 1a. In this spectrum, the following five signals were identified: I- $g_1 \approx 1.60$, $g_2 = 1.72$; II- $g_3 = 1.81$; III- $g_4 = 1.96$; IV- $g_5 = 2.00$; V- $g_6 > 2.1$. Only signals I–III were found to exhibit behavior related to the pretreatment conditions. Signal IV was very small in most cases while signals with $g > 2.1$ ("signal V") occurred only occasionally. Signals I–III were readily observable at room temperature but a significant intensity gain—without relevant changes in the intensity ratio—was obtained by recording the spectra at 123 K.

After the metathesis reaction was performed over the activated W10 sample (characterized by spectrum A) a suppression of signal I and a slight increase of signal III could be observed (spectrum B, Fig. 1b). This spectrum also appeared (with minor variations concerning the feature at $g \approx 1.53$) after various other procedures, e.g.,

TABLE I

Specific Metathesis Activities and W(V) Spin Concentrations of WO_3/Al_2O_3 Catalysts After Selected Pretreatment Procedures

Catalyst	Pretreatment	T_N (s^{-1})	Spin concentration ($10^{17} g^{-1}$)	Reduction extent (%)	Spectrum
W4	Ar, 1143 K	—	1.4	0.15	G
	Ar, 1143 K/propene, 573 K	0.65	$\ll 1.0$	$\ll 0.1$	H
	Ar, 1143 K/propene, 573 K/HCl, 298 K	—	6.7	0.70	N
W7	Ar, 1143 K/propene, 573 K	0.39	8.7	0.50	F
W10	Ar, 1073 K	—	8.2	0.30	A
	Ar, 1073 K/propene, 573 K ^a	0.37	10.0	0.38	B
	Ar, 1073 K/propene, 573 K/HCl, 298 K	—	33.7	1.25	I
	Ar, 1073 K/propene, 573 K/HCl, 298 K/HCl, 400 K	—	15.3	0.57	K
	Ar, 1073 K/HCl, 298 K/propene, 573 K	0	13.4	0.50	L
	Ar, 1073 K/H ₂ , 973 K/propene, 573 K	0.15	25.0	0.95	C
	Ar, 1073 K/H ₂ , 973 K/Ar, 1073 K/propene, 573 K	0.39	13.0	0.49	(C) ^b
	Moist air, 823 K ^c	0.003	4.3	0.15	E
	Dry air, 823 K	0.02	n.d.	n.d.	D

Note. $b = 273 \pm 5 g g^{-1} h^{-1}$; spin concentrations reported for the total of signals I and II.

^a $b = 295 g g^{-1} h^{-1}$.

^b Spectrum not shown, but analogous to spectrum C.

^c $b = 56 g g^{-1} h^{-1}$.

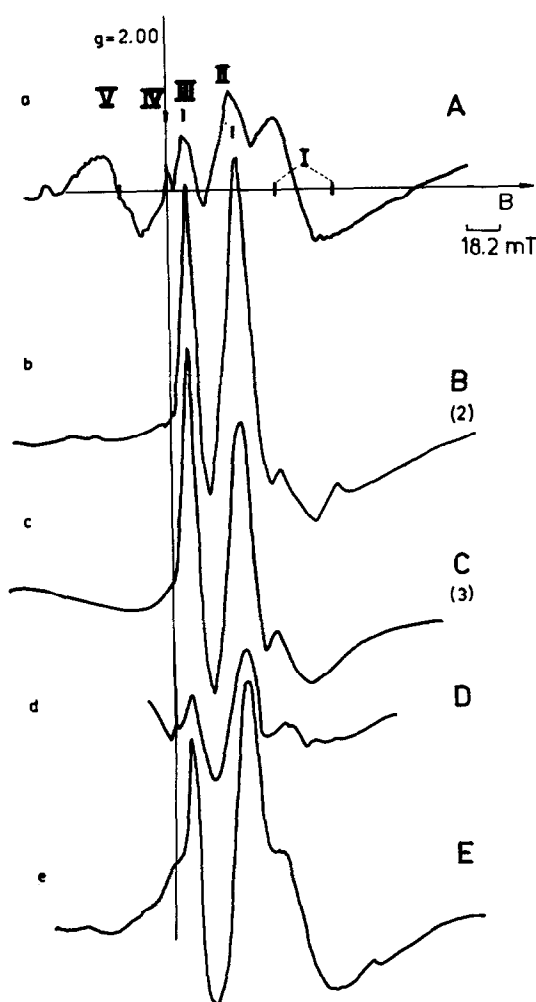


FIG. 1. X-band EPR spectra of W10 recorded at 123 K. Samples previously oxidized in air at 823 K and manipulated in the atmosphere. Pretreatments: (a) 2 h Ar 1073 K (A); (b) 2 h Ar 1073 K, 30 min propene, 573 K (B); (c) 2 h Ar 1073 K, 2 h H₂ 973 K, 30 min propene 573 K (C); (d) 2 h dried air 823 K, 30 min propene 573 K (D); (e) 2 h moist air (≈ 2.5 vol% H₂O) 823 K, 30 min propene 573 K (E). Spectra reduced by factors given in parentheses.

after reduction of the activated catalyst (characterized by spectrum A) in H₂ at 973 K for 2 h, after performing the metathesis reaction over this sample (spectrum C, Fig. 1c), after inserting another thermal treatment in Ar (1073 K, 1 h) instead of the metathesis reaction, and again after perform-

ing the metathesis reaction over the Ar-treated surface. The variation of the signal intensity due to these treatments and their effect on the metathesis activity were quite significant but opposite to each other (Table 1).

Also, the question whether the interaction of propene with the oxidized surface at 573 K may induce EPR signals was investigated. Indeed, signals I–III appeared (Figs. 1d and 1e, spectra D, E) although with a somewhat lower intensity than after the activation step in Ar. It should be noted that signal I is quite distinct now even after the metathesis reaction, in particular with a sample previously oxidized in moist air (spectrum E). The metathesis activity of the oxidized catalysts was low; after treatment in moist air it was hardly detectable.

In Fig. 2, EPR spectra of catalysts with lower WO₃ contents (after Ar, 1143 K, 2 h) are presented. It is obvious that signals I and II decrease more drastically at low WO₃ content than signal III, which becomes predominant in W4 (spectra G, H; cf. spectra A, B). With W7, signal I is weak, while it is completely absent with W4.

Interaction with HCl. It has been reported in the literature that the interaction of reduced MoO₃/Al₂O₃ catalysts with HCl at room temperature effects a considerable increase in the Mo(V) signal intensity and changes of the *g*-tensor components (22). When the W10 and W4 samples were contacted with HCl at room temperature after the completion of the metathesis reaction the overall intensity also increased and changes in the intensity ratios between the individual signals could be noted (spectra I, Fig. 3a, and N, Fig. 3e, compared with spectra B and H). The *g*-values observed, however, were those of the signals obtained without interaction with HCl, e.g., in spectrum A. Signals II and III showed the same behavior with both catalysts (II enhanced, III suppressed by HCl) but the tendencies exhibited by signal I were complex (decreasing with W10 but appearing with W4).

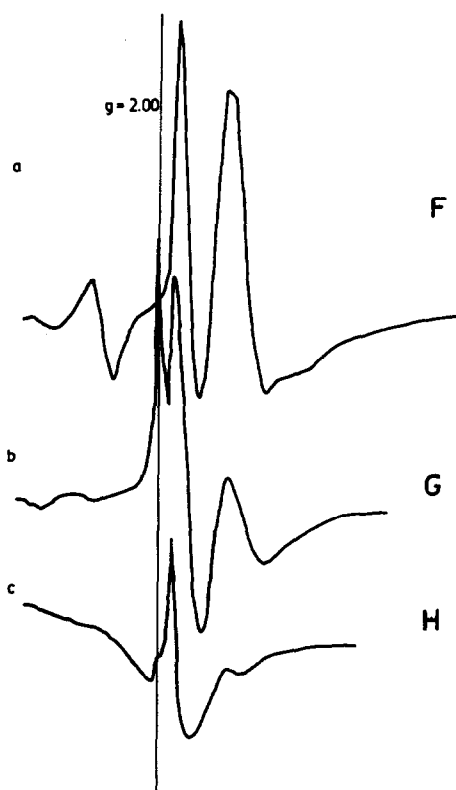


FIG. 2. X-band EPR spectra of W7 and W4 recorded at 123 K. For sample history see Fig. 1. Pretreatments: (a) W7, 2 h Ar 1143 K, 30 min propene 573 K (F); (b) W4, 2 h Ar 1143 K (G); (c) W4, 2 h Ar 1143 K, 30 min propene 573 K (H).

After an additional HCl treatment of the W10 sample at 400 K signals I and III disappeared almost completely and the total signal intensity decreased considerably (spectrum K, Fig. 3b). Spectrum L shows a situation where for W10 the order of metathesis and HCl treatment had been reversed, i.e., the metathesis had been performed on a HCl-treated surface. The ratio of signals I to II is very close to that found without HCl treatment (spectrum B) but the catalysts proved to be completely inactive. The interaction of the oxidized surface with HCl at room temperature gave rise to signals I to III though with lower intensity than with activated samples (Fig. 3d, spectrum M).

The g -factors of signals I to V are listed in Table 2.

DISCUSSION

1. Assignment of signals. The discussion will concentrate upon signals I to III. Signal IV obviously is an unresolved O_2^- signal. We assume that residual O_2 traces in the

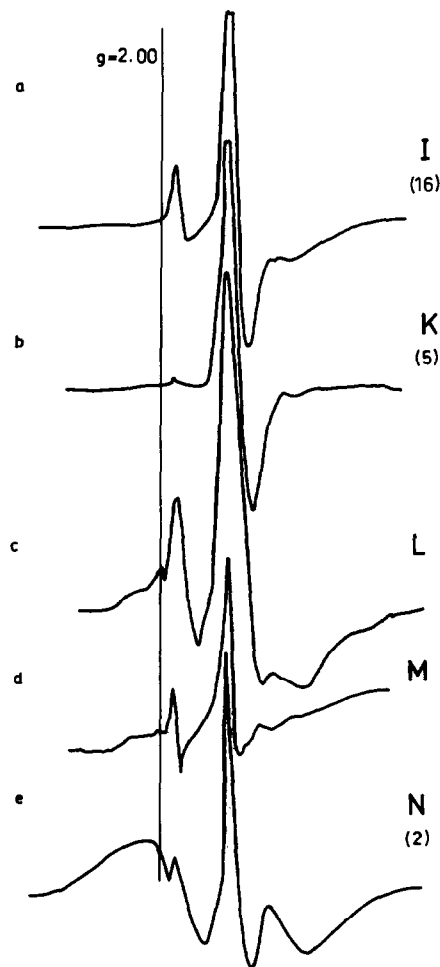


FIG. 3. X-band EPR spectra of samples treated with HCl (recorded at 123 K). For sample history see Fig. 1. Pretreatments: (a) W10, 2 h Ar 1073 K, 30 min propene 573 K, 15 min HCl 298 K (I); (b) W10, 2 h Ar 1073 K, 30 min propene 573 K, 10 min HCl 298 K, 15 min HCl 400 K (K); (c) W10, 2 h Ar 1073 K, 15 min HCl 298 K, 30 min propene 573 K (L); (d) W10, 2 h dried air 823 K, 15 min HCl 298 K (M); (e) W4, 2 h Ar 1143 K, 30 min propene 573 K, 15 min HCl 298 K (N). Spectra reduced by factors given in parentheses.

TABLE 2
g-Tensor Components of EPR Signals Observed for
Reduced WO₃/Al₂O₃ Catalysts

Signal	g_{\perp}	g_{\parallel}	Assignment	Remarks
I	1.722 ± 0.003	1.60 ± 0.02	W(V) <i>D</i> _{4h} or <i>C</i> _{4v} bridged	Spectrum A
II	1.810 ± 0.003	(1.64) ± 0.02	W(V) <i>D</i> _{4h} or <i>C</i> _{4v} isolated	g_{\parallel} determined with an HCl- treated sample (spectrum K)
III	1.960 ± 0.003	1.89 ± 0.03 ^a	Mo(V) (+ W(V) ?)	Spectrum H
IV		2.00	O ₂ ⁻	Intensity uncharacteristic
V		>2.10	Accidental paramagnetic impurities	Neither g nor intensity reproducible

^a Due to superposition with residual signal II.

sample tube (due to incomplete replacement of air) are the origin of the O₂⁻ species, which may be formed by contact with reduced parts of the surface as was shown for molybdena catalysts (31). The irreproducible "signal V" arises probably from minor impurities (e.g., Fe³⁺ containing particles) that happened to get into the sample during its prior handling, e.g., in the muffle furnace.

The g -values of signal III (where g_{\parallel} is of lower accuracy due to the superposition of a residual signal II, see spectrum H, Table 2) are close to the parameters reported by many authors for Mo(V) on SiO₂ and Al₂O₃ (21, 22, 32–34), among them values measured on our spectrometer (15 wt% MoO₃/Al₂O₃, H₂, 773 K: g_{\perp} = 1.955, g_{\parallel} = 1.88 (34)). Recently, Fricke *et al.* (25) have shown that traces of molybdenum can seriously perturb EPR measurements with tungsten systems because of the higher reducibility of Mo(VI). Figure 4 shows a spectrum obtained with a Mo-doped sample (12 wt% WO₃, 590 ppm Mo) after a pretreatment somewhat less severe than that leading to spectrum B. It is clear that signal III dominates the spectrum. We, therefore, assign signal III to the Mo impurity.

Nevertheless, the high intensity brought

about by traces of molybdena requires some explanation. A comparison of the maximum spin concentrations measured with the Mo content of the sample (e.g., for W10, 2–3 · 10¹⁷ spins/g versus 20–30 ppm ≅ 1.3–1.9 · 10¹⁷ Mo atoms/g) shows that both are, within the wide limits of uncertainty of the methods employed, in the same order of magnitude. The extensive reduction of Mo(VI) to the pentavalent state by the thermal treatments or during the metathesis, which is implied by this result, seems to be in contradiction to the high resistance of Mo(VI) to reduction found for MoO₃/Al₂O₃ catalysts with low MoO₃ content in the literature (35). However, it has also been shown that MoO₃/Al₂O₃ catalysts always contain a small fraction of Mo(VI) that can be reduced at low temperatures (35, 36) or by thermal treatments (36). We assume that on a surface occupied predominantly by tungstate species, which interact far more strongly with the Al₂O₃ surface (15, 35, 36), the Mo(VI) must put up with sites of low stabilization, which would explain its reducibility.

We cannot, of course, establish an unequivocal relation between the Mo(VI) content of the samples and the intensity of sig-

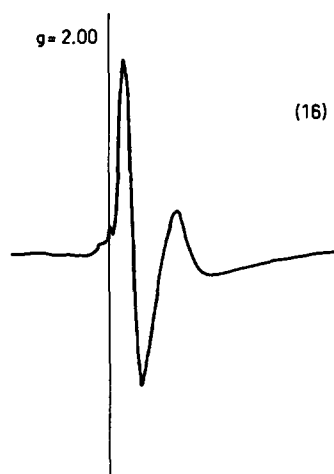


FIG. 4. X-band EPR spectrum of a catalyst containing 12 wt% WO₃ and 0.089 wt% MoO₃ (590 ppm Mo). Pretreatment: 4 h Ar 973 K, 30 min propene 573 K.

nal III. As an example, the spin concentration measured with the Mo-doped catalyst ($1.3 \cdot 10^{18}$ spins/g at a Mo content of 590 ppm $\approx 3.8 \cdot 10^{18}$ Mo atoms/g) may indicate a smaller reduction degree but could also arise from a sample partially reduced to below the 5+ state. Hence, we cannot rule out the possibility that an additional tungsten-derived signal may be hidden under signal III either. However, we would not expect such a signal to be due to W(III) as suggested by the conclusions drawn in (26–28) for this would contradict several observations reported above (e.g., its predominance in W4 where even W(V) is formed in very small quantities). Clearly more work is necessary to settle this point.

The g -values of signals I and II differ from the data given in (24) but are close to those found in (25) for W(V) in heteropoly acids and for a surface tungstate unit ($g_{\perp} = 1.783$, $g_{\parallel} = 1.68$). The presence of two signals in this region suggests that species of different coordination geometries are detected.

The coordination of W(VI) supported on Al_2O_3 has been a matter of controversy for a long time, with bridged octahedral (37) and tetrahedral (16, 38) surface tungstate species claimed for the range of WO_3 contents relevant to this study. Recent XANES and Raman results by Horsley *et al.* (39) confirm the view that samples of low WO_3 content almost exclusively contain tetrahedrally coordinated species (monomers and dimers) while octahedral species (and even small amounts of WO_3 weakly interacting with the support (40)) appear at higher loadings but still below the monolayer coverage. The literature on the reduction of $\text{WO}_3/\text{Al}_2\text{O}_3$ systems (15, 16, 35) suggests that the reducibility of these species decreases from octahedral to tetrahedral, from bridged to isolated entities.

Nevertheless, we cannot automatically assign signals I and II to octahedral and tetrahedral species as the low reducibility of tetrahedral tungstate species may preclude their observation by EPR. Indeed, an anal-

ysis of the g -values (Table 2) within the framework of ligand field theory suggests that both signals should originate from species of distorted octahedral or square pyramidal geometry: As both signals are readily observed at room temperature as well as at 123 K the ground state should be nondegenerate in both cases, which may be realized in D_{4h} (contraction along the z axis), in C_{4v} (unequal distortion along z or removal of one ligand), and in D_{2d} species as well. The last case would, however, yield $g_{\parallel} \approx 2.0$ (ground state d_{z^2}) or $g_{\parallel} > g_{\perp}$ and must, therefore, be discarded.

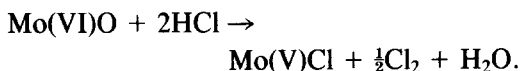
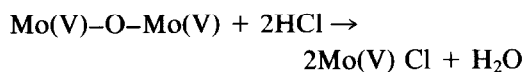
Values of the ligand field stabilization energy $10D_q$ for W^{5+} in an oxidic environment ($=\Delta E_{\parallel}$ for D_{4h} contracted along z , or C_{4v}) may be derived from the g -values of Table 2, with the covalent contributions taken into consideration by an orbital reduction factor of 40% (41). They amount to $\approx 30,000$ cm^{-1} (signal I) and $\approx 37,500$ cm^{-1} (signal II). This can be compared to values obtained from measurements of the static susceptibility of WOX_5 compounds ($X = \text{F}, \text{Cl}, \text{I}$, $10D_q = 23,000\text{--}37,500$ cm^{-1}) (42) and supports our assignment although it should be kept in mind that g_{\parallel} of signal II could be determined only after treatment with HCl. The transition energies for the perpendicular component are $\approx 10,700$ cm^{-1} (I) and $\approx 15,700$ cm^{-1} (II), which yields a nearly equal tetragonal distortion ($\Delta E_{\parallel} - \Delta E_{\perp}$) for the two species. The higher ligand field stabilization energy of species II may indicate a stronger bond between the central ion and the oxygen ligands, i.e., a decreased reducibility than that of species I.

This conclusion is confirmed by the spectra obtained with W10 where any reductive treatment (H_2 at 973 K, propene at 573 K, HCl at 298 and 400 K, *vide infra*) of the sample activated in Ar (spectrum A) results in a decrease of signal I relative to signal II (spectra B, C, I, K). Hence, any gain in overall intensity is predominantly due to signal II while a decrease of the absolute intensity may be deduced for signal I in several cases. Certainly, the W(V) state is an

intermediate one and can be transformed to lower oxidation states. Thus, the behavior of signal II appears to be determined by the W(V) formation while with signal I the W(V) consumption may already prevail under the given conditions, which would imply a higher reducibility of this species.

On this basis we would tentatively assign signals I and II to species of D_{4h} or, more probably, of C_{4v} symmetry, with signal II derived from isolated structures and signal I from bridged ones. Both species are most probably a small minority among the predominating tetrahedral structures. The isolated species may be W(V) located at alumina cation sites or split off from bridged structures during the reduction process. The increased reducibility of the bridged structures agrees with the reducibility tendencies mentioned above. The somewhat surprising observation that signal I appears with the oxidized W10 sample (spectra D, E) after a procedure that effects its suppression on the activated one (573 K, propene; spectra B, A) may lend additional support to our assignment since it is known that tetrahedral tungstate species may be converted into octahedral ones by the coordination of water molecules (39). This should be the case when a sample is treated with moist air or when an air-treated sample, which presumably contains adsorbed oxygen (30), is contacted with propene, and may lead to an increased amount of bridged structures (species I) on the surface. On the other hand, it is also possible that the behavior of signal I is governed by general differences in the reducibility of hydroxylated and dehydroxylated surfaces.

2. *Interaction of reduced WO_3/Al_2O_3 catalysts with HCl.* According to Abdo *et al.* (22) the interaction of HCl with reduced or unreduced MoO_3/Al_2O_3 induces ligand exchange processes, which release water molecules and are accompanied by the cleavage of Mo–O–Mo bridges and the reduction of Mo(VI), e.g.,



In our experiments, an increase of the signal intensity similar to that reported for the Mo system was observed for signal II. On the other hand, we did not find any shift in g_{\perp} on HCl treatment while an apparent shift of g_{\perp} was obtained with MoO_3/Al_2O_3 due to the reversal of the g -factors not resolved in the X-band (22). Instead, our results reveal complex changes of the signal intensities which indicate a superposition of several effects. However, the details of the operating mechanisms are not yet known.

Among the effects expected from the interaction of HCl with a WO_3/Al_2O_3 surface only the reductive effect was unambiguously proved. This refers not only to spectrum M induced from an oxidized surface but also to the suppression of the Mo impurity signal (III) at room temperature and of all signals at 400 K. It seems surprising that HCl exerts a reductive effect on a surface that withstands a severe H_2 treatment (cf. spectra B and C) but it is well known from the sulfidation of MoO_3/Al_2O_3 and of CoO/Al_2O_3 catalysts that the reduction is greatly facilitated when the oxygen ligands can be replaced by ligands providing an increased covalent interaction with the central ion (43).

On the other hand, no evidence for this ligand exchange can be derived directly from the spectra under discussion. The invariance of the g_{\perp} parameters under the HCl treatment implies that the extent of a ligand exchange should be small in any case. However, the complete deactivation of the catalyst by the previous interaction with HCl, which is accompanied by an increased contribution of signal I to the corresponding spectrum L (compare with spectrum I), may be understood as an indication that the exchange processes have taken place. The introduction of chlorine into the coordination sphere of W would not a priori be expected to exert a deleterious influence on the metathesis activity as chlorine-containing homogeneous metathesis catalysts

are well known, but the water released is an effective poison, and its quantity may be significant when the tetrahedral majority of sites is involved in the exchange processes. The increased contribution of signal I after the subsequent metathesis at 573 K (spectrum L) may be seen as an analogy to the results obtained with the oxidized samples (in particular, spectrum E) and, hence, as a confirmation of the assumption that water is present on the surface as a consequence of ligand exchange processes.

In the course of these ligand exchange processes the cleavage of W–O–W bridges should be possible but it should operate on paired W(V) structures as well as on W(VI) and W(VI)/W(V) pairs. If the bridged structures include more than two octahedral units situations may be constructed where an enhancement of signal II and a decrease as well as an increase of signal I may be predicted. We prefer the view that the appearance of signal I in the HCl-treated W4 sample (spectrum N) is due to the generally higher interaction between the tungstate entities and the support at lower loadings. This would render part of the (minority) octahedral sites accessible to reduction only if ligand exchange can proceed simultaneously. In conclusion, the interaction of HCl with $\text{WO}_3/\text{Al}_2\text{O}_3$ surfaces includes a significant contribution of reduction processes that mask the possible decoupling of paired structures.

3. *The relevance of W(V) for the metathesis reaction.* In Table 1, the metathesis activities obtained with catalysts of varying WO_3 content and after different catalyst pretreatments are compiled together with the spin concentrations measured. It can be seen that no correlation between the specific activities (turnover numbers, T_N) and the spin concentrations exists even if the HCl-treated samples are included. The most convincing argument for this is the high specific activity of W4, which does not show signal I and shows only weak signals II and III. Essentially the same applies to the spectra recorded before metathesis; i.e., W(V) is also excluded as a precursor

state. The inclusion of signal III in the intensity calculations would not alter the situation.

Further evidence is supplied by some reductive and oxidative treatments performed with W10 (Table 1, lines 10–13). A reduction of the catalyst at 973 K increases the amount of W(V) but lowers the activity. An additional thermal treatment that leads to an increase in activity, obviously by removing chemisorbed hydrogen, has the opposite effect on the spin concentration. Finally, signals I–III can be observed in intensities not too much below those obtained on the active surface on a completely inactive one (pretreatments in air).

We conclude, therefore, that W(V)/ Al_2O_3 as a whole and any of its forms as detected in this study are of no relevance to the metathesis reaction but are formed as a by-product during the activation processes and the metathesis reaction itself. The inverse correlation of the specific activity with the reduction extent or, more generally, with the reducibility (14) suggests that the active sites are formed starting from W(VI) precursors. This view will be substantiated by a more comprehensive catalytic study in part III of this series.

CONCLUSIONS

During the activation of $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts for the metathesis reaction, which includes thermal treatments in flowing inert gas at temperatures ≥ 973 K, and during the metathesis reaction itself a small proportion of the W(VI) is reduced to W(V). The pentavalent tungsten gives rise to two EPR signals ($g_{\perp} = 1.722$, $g_{\parallel} = 1.60$; $g_{\perp} = 1.810$, $g_{\parallel} \approx 1.64$). Mo impurities difficult to avoid in this system cause a third signal ($g_{\perp} = 1.960$; $g_{\parallel} = 1.89$), which may mask a further W(V) species. The problem of Mo impurities may be of general significance for EPR work on W-based systems. Any relevance of the observed W(V) species to the metathesis of propene was excluded in view of the catalytic activities obtained.

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