Propene Metathesis over Silica-Supported Tungsten Oxide Catalyst—Catalyst Induction Mechanism

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The propene metathesis reaction was studied from the point of view of elucidating the mechanism of catalyst induction and establishing conditions for maximum activity. Instrumental techniques such as ESR, IR, and TPD were used to study the various aspects. During catalyst induction, trace quantities of acetone and acetaldehyde were detected in the product stream, indicating that lattice oxygen from tungsten oxide might be responsible for these products. Induction appeared to proceed via two steps since pretreatment of the catalyst with nitrogen and hydrogen yielded a decreased amount of acetone in the latter case whereas acetaldehyde remained unaffected. ESR studies indicated some interaction between tungsten oxide and silica at the catalyst preparatory stage as well as stabilisation of reduced tungsta species on the catalyst after its use and regeneration. Catalyst activity appeared to depend on conditions of pretreatment. Change in nitrogen pretreatment temperature from 500 to 600°C resulted in transition from strong to negligible external mass transfer behaviour of the catalyst. TPD studies in this context showed possible loss of lattice oxygen from tungsten oxide under the above-mentioned conditions of catalyst pretreatment. ESR studies indicated the reduction of WO_3 to a nonstoichiometric oxidation state. Hence catalytic activity appears to be related to the nonstoichiometric state of tungsten oxide, which may be $WO_{2.9}$ (as deduced from the blue-violet colour of the used catalyst). © 1991 Academic Press, Inc.

INTRODUCTION

Silica-supported tungsta catalysts appear to be promising for the metathesis of propene (*1*):

$$2C_3H_6 \rightleftarrows C_2H_4 + C_4H_8$$
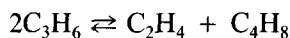
This catalyst has been reported to exhibit interesting behaviour, viz., anomalous external mass transfer behaviour (*2*) and induction effect (*3*) dependent on the mode of catalyst pretreatment or activation. Differences in kinetic mechanism have been reported. Whereas the data of Begley and Wilson (*4*) as well as that of Gupta and Mann (*5*) support a single-site Eley–Rideal mechanism, the data of other researchers favour a dual-site Langmuir–Hinshelwood surface reaction controlling step mechanism (*6, 7*) or a nonpairwise carbene mechanism (*8*). Induction periods (i.e., the time required by a certain catalyst system to achieve a steady state activity), ranging from a small undetectable period to about 24 h or more, have been reported for this reaction system (*3*). Studies by Fathikalajahi *et al.* (*9*) reveal that induction apparently proceeds via the following two successive steps: reduction of tungsten oxide and formation of a suspected metallocarbene species.

Choung and Weller (*10*) have shown that some intermediate nonstoichiometric oxidation state of tungsten oxide could be the most active one for propene metathesis since pretreatment of the catalyst with nitrogen was found to be more beneficial than pretreatment with oxygen or hydrogen in their studies.

Appearance of anomalous external mass transfer behaviour has been reported by Moffat *et al.* (*2*) and Luckner and Wills (*3*). The former has proposed site localised diffusional limitations as an explanation, whereas Pennella (*11*) attributes pressure

fluctuations in the feed purification unit of their setup to be responsible for this behaviour. The present work is part of a Ph.D. thesis (12) aimed at investigating the induction and mass transfer behavior of silica supported tungsta catalysts.

EXPERIMENTAL

The reaction was studied in a single pass continuous flow system using a tubular stainless steel 316 reactor of dimensions 17.5 mm outer diameter, 15 mm inner diameter, 765 mm length, operated under conditions approximating plug flow. The reactor was mounted with a coaxial thermowell, the height of which was adjustable to monitor temperature along the length of the catalyst bed. The reactor was loaded with a maximum of 3 g of catalyst in order to ensure isothermality. The feed, a propene (90%)–propane (10%) mixture, was dried over activated molecular sieve 4 Å. Analysis of the product stream was carried out using a gas chromatograph fitted with a 3 m × 3 mm stainless steel column containing 80–100 mesh n-octane-coated Poracil-C. A FID detector was used.

A catalyst consisting of 20 wt% tungsten oxide on silica was prepared by impregnating catalyst grade silica gel (grade 979 of Davison Chemicals, Pennsylvania), having BET surface area of 300 m²/g, with an aqueous solution of ammonium paratungstate from Fluka. Just enough demineralised water was taken for complete dissolution of the paratungstate. The mixture had to be heated for complete dissolution of the salt. The required quantity of silica gel catalyst was evacuated of air by using vacuum and the solution was poured over it. Excess solution was evaporated using vacuum. The catalyst was then dried in an oven at 110°C for 12 h before being calcined at 600°C for 8 h, while the temperature was raised 1°C per min up to 250°C. This temperature was maintained for 2 h and then raised 3°C per min up to 600°C. The final form of the catalyst used for the entire study was particles of average

diameter 0.35 mm having BET surface area 240 m²/g.

Reduction of tungsten oxide to nonstoichiometric oxidation states, in the process of its catalysing the metathesis of propene, is well documented in the literature (3, 9). However, detection of oxygenated species of propene, which are likely to form during this step, has not been reported. Therefore atempts were made to detect possible formation of such species. Two sets of experiments were performed to ascertain the existence of a second step subsequent to reduction of the tungsten oxide, which is believed to be the first step as highlighted by the work of Fathikalajahi et al. (9). In the first set, a fresh catalyst sample was activated in air at 600°C for 2 h and then purged with pure dry nitrogen at 600°C for 30 min. The temperature was then reduced to 550°C in nitrogen flow before switching over to propene. The product stream, during the first 30 min of reaction, which corresponded to the induction period, was bubbled through cold spectroscopic grade CCl_4. In the second set of experiments the catalyst was activated in hydrogen at 600°C for 2 h before being purged with nitrogen at 600°C for 30 min cooled to 550°C and switched over to propene. It was initially determined that the tungsten oxide component of the catalyst had undergone reduction on treatment with hydrogen at this temperature.

In addition to other observations, silica-supported tungsta catalyst has been reported by Moffat et al. (2) to exhibit strong interphase mass transfer behaviour which has been described as anomalous because of the high activation energy associated with the reaction in spite of strong diffusional limitations across the gas–liquid interphase.

In the present work the influence of interphase mass transfer was studied under two different conditions of catalyst activation. Two sets of experiments were carried out which differed only in the temperature of activation of the catalyst. This was deemed necessary in light of Moffat et al.'s work (2), where it is suspected that this catalyst

system exhibits probable surface heterogeneity. In one set of experiments the catalyst was activated in nitrogen at 500°C for 2 h before switching over to propene, whereas in another set the nitrogen activation temperature was 600°C for 2 h followed by cooling in nitrogen to 500°C before switching over to propene. All the experiments were performed at a constant reaction temperature 500°C and constant space time 0.33 g cat h/g mole propene. However, the flow velocity of propene was varied over the range 2.8 to 30.3 cm/s at constant space time by manipulating the weight of catalyst and the molar flow rate of propene for different experiments in each set. Hence, in principle, the effect of reactant flow velocity on the conversion of propene at constant space time and reaction temperature was studied for two sets of experiments which differed only in the catalyst activation temperature.

Temperature-programmed desorption (TPD) studies were carried out to explain the results of the interphase mass transfer study carried out in the present work. These studies were carried out in the reaction assembly by attaching a thermal conductivity detector in line for detecting desorbed species. The carrier gas flow rate, as well as the temperature programming, was the same as that during catalyst pretreatment, i.e., 500 ml/min and 15°C/min, the temperature being held at 600°C for 2 h after attainment of this temperature. Both pure dry nitrogen and hydrogen were used as carrier gases. The samples were heated at 200°C in a stream of carrier gas for 30 min to remove free water before running the experiment. The aim of the TPD studies was to determine whether nitrogen activation could reduce the tungsten oxide component of the catalyst to nonstoichiometric states.

Electron spin resonance spectra were recorded on a Varian 400 Endor instrument at room temperature (~30°C) because negligible line broadening was observed when compared to spectra taken at liquid nitrogen temperature. TCNE with a g value of 2.00277 was used as the marker. The samples were cooled to room temperature in a flow of nitrogen before transferring them to a sample tube. At this stage the samples were momentarily exposed to the atmosphere, but experiments using sealed tubes did not show appreciable change in the signals. The effect of temperature and duration of activation of the catalyst in nitrogen on the activity of the catalyst was also studied.

RESULTS AND DISCUSSION

The infrared spectroscopic study was restricted to a qualitative one. Formation of both acetone and acetaldehyde at the stage of catalyst induction was detected by the IR study, in both prereduced and unreduced catalyst samples. The intensity of IR bands for acetone was found to markedly decrease in the catalyst sample prereduced in hydrogen at 600°C for 2 h, as compared to the unreduced sample which was activated in air at 600°C and purged with nitrogen before the metathesis reaction was run. This can be seen by comparing the IR bands in Fig. 1. In the case of the unreduced sample about 30 to 40% of propene was observed to adsorb irreversibly on the catalyst during the first few minutes of the reaction as deduced from the GLC analysis. The results pertaining to the study of external mass transfer behaviour of the catalyst are tabulated in Table 1. These results were obtained in the steady state regime, which followed the catalyst induction step. The isothermal interphase effectiveness factor $\bar{\eta}$ was calculated as the ratio of conversion of propene under conditions of measurable external mass transfer effect to that when this effect was negligible. A comparison of the values of $\bar{\eta}$ as a function of the reactant flow velocity (Table 1) shows a steady increase in $\bar{\eta}$ with flow velocity, indicating that the reaction is limited by strong resistance to external mass transfer. In this case the catalyst was activated in nitrogen at 500°C for 2 h before the metathesis reaction was run at 500°C. However, on activation of the catalyst at 600°C for 2 h prior to propene metathesis, $\bar{\eta}$ remained uninfluenced by flow velocity as can be observed by the constancy of $\bar{\eta}$ val-
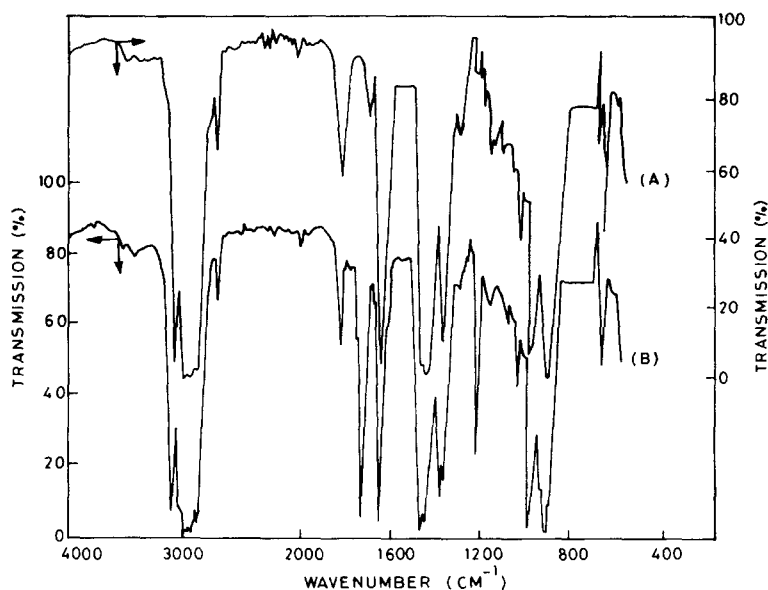
FIG. 1. IR spectra of product stream in the case of unreduced catalyst (A) and prereduced catalyst (B). Bands for acetone at 3530, 3440, 1757, 1725, 1225 cm^{-1}; bands for acetaldehyde at 3530, 3440, 2740, 1725, 1370 cm^{-1}.

ues at 600°C, which indicates a negligible resistance to interphase mass transfer. The results of additional experiments aimed at studying the effects of activation temperature of the catalyst in nitrogen medium on the activity of the catalyst are presented in Table 2. These experiments were carried out at temperature 500°C and space time 0.33 g cat h/g mole propene, which are the same as those for the mass transfer study. The

results in Table 2 reveal that catalytic activity increases as the nitrogen activation temperature is increased from 500 to 600°C but is steady thereafter. The conversion of propene and hence the activity of the catalyst also appear to be dependent on the duration of activation; a minimum activation period of 2 h at 600°C is required to obtain maximum activity (under the experimental conditions), as can be seen from the increase in

TABLE 1

Effect of Catalyst Activation Temperature on Conversion as a Function of Reactant Flow Velocity

Expt. no.	Flow velocity (cm/s)	Reynolds number	Fractional conversion at		Isothermal effectiveness factor at	
			pretreatment temperature (°C)			
			500	600	500	600
1	2.84	0.76	0.020	0.094	0.195	0.97
2	4.97	1.53	0.038	0.095	0.372	0.98
3	9.96	3.06	0.075	0.093	0.733	0.96
4	19.92	6.12	0.102	0.097	0.998	1.00
5	30.38	9.33	0.102	0.096	1.000	0.99

Note. Experimental conditions: catalyst, 20 wt% WO_3/SiO_2; space time, 0.33 g cat h/g mole C_3H_6; reaction temperature, 500°C.

TABLE 2

Conversion as a Function of Duration and Temperature of Catalyst Pretreatment in Nitrogen

Expt. no.	Conditions of catalyst pretreatment with N_2		Fractional conversion
	Temperature (°C)	Duration (h)	
1	500	2	0.020
2	600	1	0.070
3	600	2	0.090
4	650	2	0.091

Note. Experimental conditions: catalyst, 20 wt% WO_3/SiO_2; space time, 0.33 g cat h/g mole C_3H_6; reaction temperature, 500°C.

TABLE 3

Results of TPD of Silica Supports and the Catalyst WO_3/SiO_2

Expt. no.	Sample	Range and maximum of signal (°C)	Assignment
1.	SiO_2 support	70–150, broad	Desorption of free water
		385	Desorption of chemisorbed water
2.	Catalyst, 20 wt% WO_3 on SiO_2	70–150, broad	Desorption of free water
		325	Desorption of chemisorbed water
	In case of N_2 as carrier gas	600°C, broad elutes over a period of 2 h	May be due to loss of lattice oxygen from WO_3 leading to formation of tungsten oxides of nonstoichiometric oxidation states
	In case of H_2 as carrier gas	550°C, broad	

conversion when the duration of activation is raised from 1 to 2 h at 600°C (Table 2). The results of TPD runs are presented in Table 3 and also in Fig. 2. Curve A is for the silica support with hydrogen as carrier gas, whereas curves B and C are for the WO_3/ SiO_2 catalyst samples with hydrogen and nitrogen as carrier gases, respectively. Comparison of curve A in Fig. 2 with curves B and C shows the existence of signals in the temperature range of 550 to 600°C in the latter two cases. This signal, which is absent

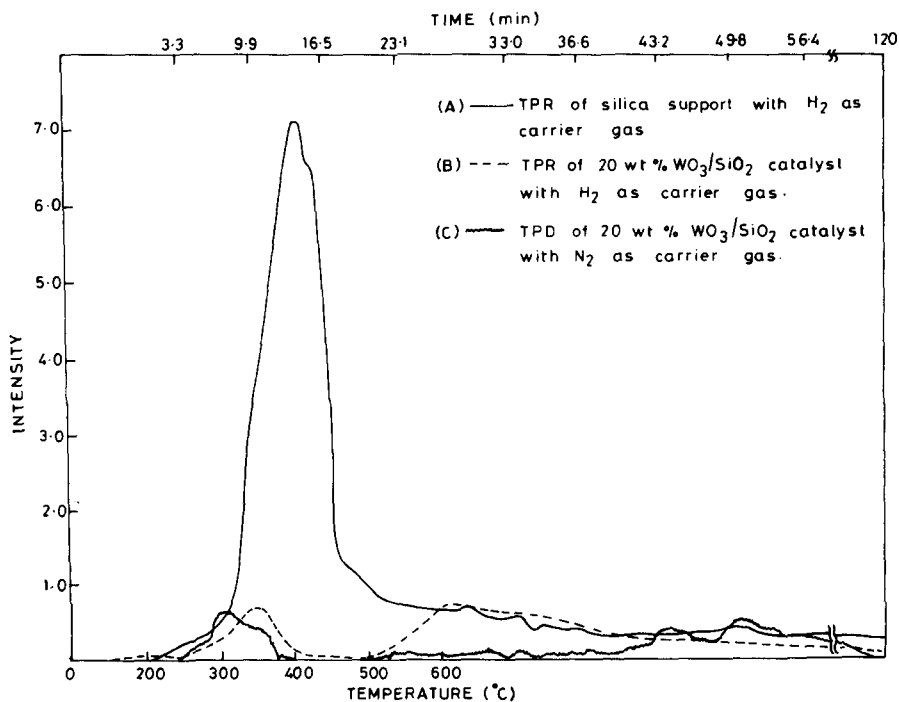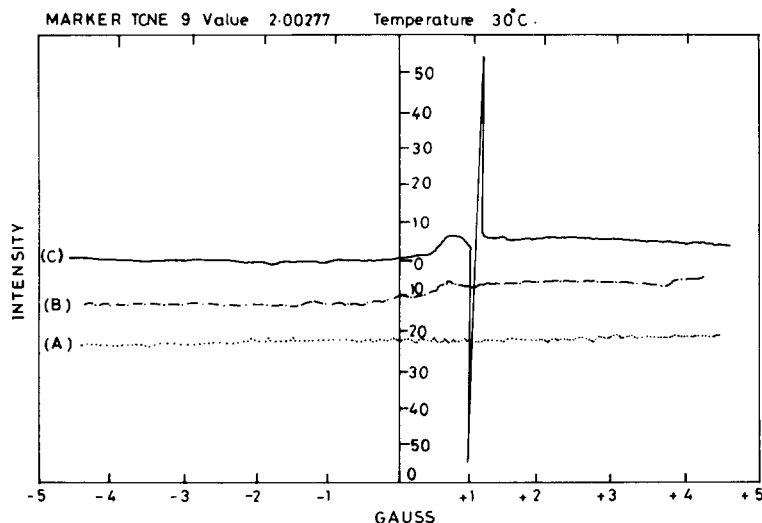FIG. 2. TPD patterns of SiO_2 support and 20% WO_3/SiO_2 catalyst.

MARKER TCNE 9 Value 2·00277   Temperature 30°C·

FIG. 3. ESR spectra of (A) pure WO_3; (B) freshly prepared 20% WO_3/SiO_2 catalyst; (C) 20% WO_3/SiO_2 catalyst after catalysing propene metathesis at 500°C. Scan range, 2000 G; time constant, 0.128 s; modulation amplitude, 10 × 1 G; receiver gain, 10 × 10^2 × 10; field set, 3200 G; scan time, 8 min; modulation frequency, 100 kHz; microwave frequency, 9.5 GHz.

in the case of the SiO_2 support (curve A), begins to appear at 550°C when the carrier gas is hydrogen and at 600°C when the carrier is nitrogen (curves B,C). A longer period of elution (2 h) is observed when nitrogen is used as the carrier. The catalyst also exhibits ESR signals with g values of 1.958 and 1.963 on activation in nitrogen at 500 and 600°C, respectively, and a much stronger narrower signal at $g = 2.0025$ in the case of hydrogen activation. It is therefore presumed that the signal appearing at temperatures above 550°C TPD studies corresponds to reduction of the catalyst to a non-

TABLE 4

Details of ESR Spectra of Pure WO_3, SiO_2 support, and the Catalyst WO_3/SiO_2 Subjected to Various Pretreatments

| Sample no.	Sample	g Peak width (G)
1.	Pure tungsten trioxide	No signal
2.	SiO_2 support	4.1 (weak)
3.	Fresh calcined unused SiO_2-supported WO_3 catalyst	1.997 (weak)
4.	Used catalyst, propene metathesis followed by regeneration in air at 600°C for 2 h	2.195, 980 (strong broad)
5.	Fresh catalyst treated with N_2 at 500°C for 2 h	2.195 (strong), 980 1.958 (weak), 30
6.	Fresh catalyst treated with N_2 at 600°C for 2 h	2.196 (strong), 980 1.963 (weak), 30
7.	Sample 5 after catalysing propene metathesis at 500°C	2.0025 (strong), 3.1
8.	Sample 6 after catalysing propene metathesis at 500°C	2.0025 (strong), 3.1
9.	Fresh catalyst treated with H_2 at 500°C for 2 h	2.0025 (strong), 3.1
10.	Fresh catalyst treated with H_2 at 600°C for 2 h	2.0025 (strong), 3.2
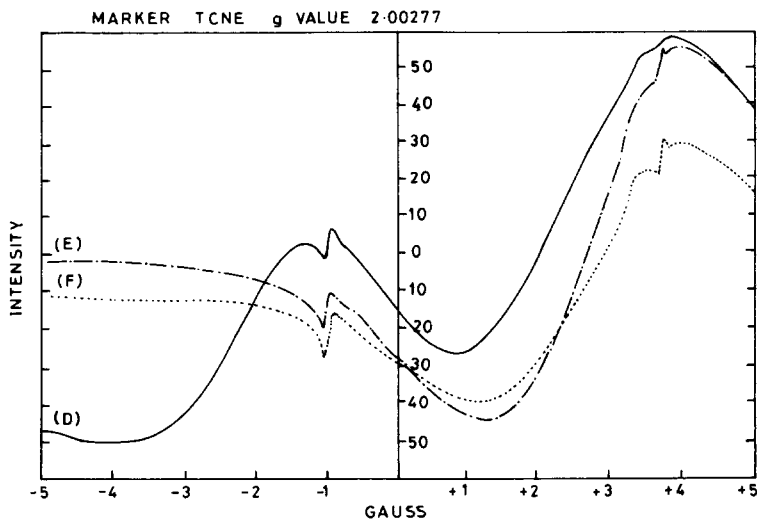
FIG. 4. ESR spectra of (D) 20% WO_3/SiO_2 catalyst after catalysing propene metathesis followed by its regeneration; (E) 20% WO_3/SiO_2 catalyst activated in N_2 at 500°C for 2 h; (F) 20% WO_3/SiO_2 catalyst activated in N_2 at 600°C for 2 h. Scan range, ×4000 G; temperature, 30°; field set, 2000 G; other parameters same as for Fig. 3.

stoichiometric oxidation state. ESR spectra of pure tungsten oxide (Fluka) and the catalyst treated in nitrogen and hydrogen as well as after propene metathesis are presented in Figs. 3–5, together with spectra of the fresh catalyst and regenerated catalyst. The results are also summarised in Table 4. The aforementioned results of various investigations throw some light on the following aspects of the reaction system.

1. Catalyst preparation. The absence of ESR signals close to a g value of 2, in the cases of both pure WO_3 and SiO_2 support (Table 3, samples 1 and 2, and Fig. 3), but the appearance of a weak signal at $g = 1.997$ in the case of the freshly prepared tungsta on silica catalyst (Table 4, sample 3, and Fig. 3, curve B), is indicative of interaction between SiO_2 and WO_3. After catalysing the metathesis of propene at 500°C, but before regeneration, the catalyst exhibits a strong narrow sharp signal at $g = 2.0025$ with a peak-to-peak width of 3.1 G (Fig. 3, curve C). This signal is characteristic of nonstoichiometrically reduced tungsten oxide. The peak width is, however, broader than that

reported in the literature (*13*). Regeneration of the catalyst in a stream of nitrogen containing 3% oxygen followed by continuation in air for 4 and 2 h respectively still shows the presence of a broad ESR signal at $g = 2.195$ with a peak-to-peak width of 980 G (Fig. 4, Curve D). The possibility of incomplete catalyst regeneration was ruled out since the regenerated catalyst yielded the same level of conversion as the fresh catalyst. The regenerated catalyst also exhibited a smaller induction period and when used for the IR study, it showed behaviour similar to that of a prereduced catalyst; i.e., a lesser amount of acetone was detected in comparison to a fresh unused catalyst. Hence it appears that at least some of the tungsten oxide that is reduced to lower states cannot be readily reoxidised to W(VI) during regeneration and thus appears to be in a stabilised nonstoichiometric state.

2. Catalyst induction. Results of the IR study (Fig. 1) show that acetone and acetaldehyde appear in the product stream during early stages of propene metathesis on WO_3/SiO_2 catalyst, suggesting a reduction of the catalyst by loss of lattice oxygen from tung-
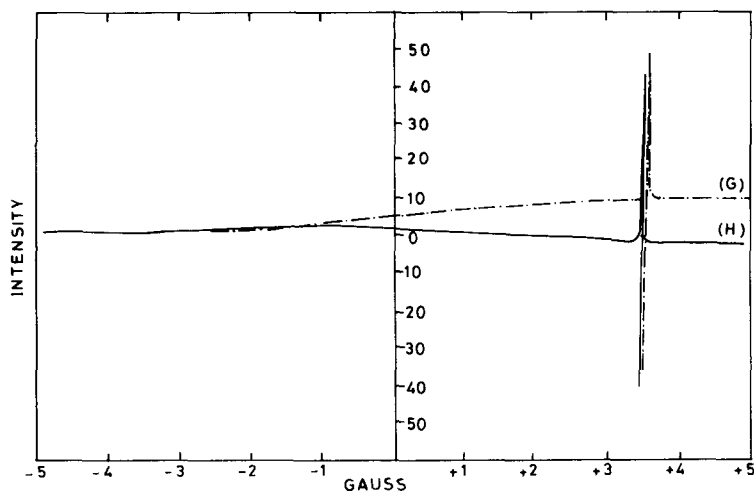
FIG. 5. ESR spectra of (G) 20% WO_3/SiO_2 catalyst activated in N_2 at 500 or 600°C followed by metathesis of propene; (H) 20% WO_3/SiO_2 catalyst activated in H_2 at 500 or 600°C. Scan range 4000 G; microwave power 5 mW; modulation frequency 100 kHz; temperature 30°C; field set 2000 G; marker tone g value 2.0027; microwave frequency 9.5 GHz; time constant 0.5 s.

sten oxide. Results of the ESR study (Table 4, samples 7,8) confirm these presumptions. A decrease in the intensity of IR bands for acetone occurred during induction in the case of a prereduced catalyst in comparison to an unreduced catalyst flushed with nitrogen before the reaction, and the persistance of induction behaviour even after prereduction of the catalyst indicates the involvement of two steps in the induction behaviour of the WO_3/SiO_2 catalyst. Since the intensity of IR bands of acetaldehyde remains unaffected even after prereduction of the catalyst with hydrogen at 600°C, its formation appears to be linked to the second step and therefore it would probably be a more reliable indication of the number of active sites than would be the formation of acetone. The following simplistic mechanism is proposed to explain the experimental results for catalyst induction:

(a) Initial reduction of the catalyst by propene yielding acetone and reduced metal oxide (Scheme 1).
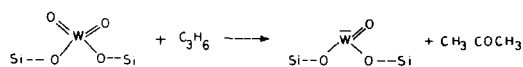
SCHEME 1

(b) Subsequent to this, simultaneous formation of a metallocarbene and acetaldehyde as a second step (Scheme 2).

SCHEME 2

The metallocarbene could then further react with propene to yield the reaction products via the nonpairwise carbene mechanism.

3. *External mass transfer behaviour.* From the results in Table 1, it is evident that the reaction is strongly limited by resistance to interphase mass transfer when the catalyst is activated in nitrogen at a temperature less than 600°C, viz. 500°C, whereas negligible resistance to mass transfer is observed on activation at a temperature of 600°C or above, under identical reaction conditions. This transition in the mass transfer behaviour simply by a change in the catalyst activation temperature from 500 to 600°C could be for either or both of the following reasons: (a) desorption of some strongly adsorbed species from the surface of the catalyst during activation at the higher temperature (600°C), which could result in

availability of previously blocked active sites, or (b) a change in the intrinsic activity of the catalyst for some reasons such as reduction of the tungsten oxide to some other oxidation state. Of these two reasons, the second one appears more probable for the following reasons:

(i) TPD results (Fig. 2, curves B and C) show that some species desorb from the catalyst in the temperature range of 550 to 600°C. This desorption is slow and is also related to the carrier stream used; e.g., when hydrogen is used as the carrier gas this signal elutes in about 1 h and elution begins at 550°C (Fig. 2, curve B), whereas with nitrogen as the carrier gas elution of this signal begins only at a temperature of 600°C and requires a period of about 2 h (Fig. 2, curve C). Simple desorption of some strongly adsorbed species would be expected to depend only on the temperature and not on the type of carrier gas used. Choung and Weller (10) have also reported that the activity of the WO_3/SiO_2 catalyst depends on the medium of activation, and that of the three, i.e., oxygen, nitrogen, and hydrogen, activation in nitrogen results in the best activity.

(ii) From Table 2 note that a minimum duration of 2 h at a temperature of 600°C is required for attainment of maximum catalytic activity; the duration matches the time required for complete elution of the signal in TPD studies using nitrogen as the carrier gas, indicating a link between the two. Also, all the catalyst samples subjected to activation in nitrogen exhibit ESR signals (Table 4, Samples 5 and 6). Therefore desorption of species, as deduced from TPD studies, appears due to a change in the oxidation state of the catalyst. Therefore it appears that the change in interphase mass transfer behaviour with a change in catalyst activation temperature is due to a change in intrinsic catalytic activity rather than to simple desorption. The interphase mass transfer study shows that the net activity of the catalyst increases with an increase in the activation temperature, since the conversion increases almost fivefold, from 0.2 to 0.9 (Table 1). However, the resistance to interphase mass transfer, which is also expected to increase with increasing catalyst activity, apparently decreases, since the conversion of propene remains uninfluenced by reactant flow velocity in the case of experiments wherein the catalyst was activated at the higher activation temperature, viz., 600°C (Table 1). This apparent contradiction can be explained as follows: The intrinsic catalytic activity can be expressed as

$$A = a_s \times N_s,$$

assuming surface homogeneity. Here A is the net catalytic activity, a_s is the activity per active site, and N_s is the total number of sites per unit mass of catalyst. The external mass transfer behaviour would be expected to be influenced to a much greater extent by a_s rather than by N_s. And a catalyst with a small number of extremely active, widely dispersed, active sites would be expected to have its activity limited by strong resistance to localised external mass transfer, whereas a catalyst with a large number of moderate to weak active sites would show negligible external mass transfer resistance under the same experimental conditions. This explanation has been proposed by Moffat et al. (2) to account for the extreme interphase mass transfer resistance exhibited by the WO_3/SiO_2 catalyst in contrast to the negligible mass transfer resistance exhibited by the MoO_3/Al_2O_3 catalyst. It is presumed that in the present work, an increase in the catalyst activation temperature from 500 to 600°C probably leads to a similar change, viz., a decrease in activity per site, with a simultaneous increase in the total number of active sites, which accounts for a simultaneous increase in net catalytic activity and a decrease in the resistance to interphase mass transfer. However, direct evidence for an increase in the number of active sites could not be achieved in this work and the explanation is purely hypothetical in nature. Other studies in support of a possible change in catalytic activity with a change in activation conditions are those of Choung and

Weller (*10*), wherein the catalyst activity appears to be related to the medium of pretreatment, and Pennella and Banks (*14*), wherein addition of ligands and polyolefins to the feed has been reported to temporarily enhance catalytic activity. It has been shown by diffuse reflectance spectroscopic studies (*15*) that the temperature for onset of propene metathesis coincides with that required for reduction of tungsten oxide. Hence a change in intrinsic catalytic activity with a change in activation temperature, as proposed in this work, needs serious attention. The color of the catalyst was observed to change from pale yellow to blue-violet after it catalysed the metathesis of propene and the oxidation state of tungsten oxide corresponding to this colour, as reported in the literature (*16*) is $WO_{2.9}$. It is difficult to distinguish between various nonstoichiometric states of tungsten oxide using ESR spectroscopy because of the existence of at least four or more such oxides with very small differences in the g values of their ESR signals (*13*).

CONCLUSIONS

Some interaction is evident between the silica support and the tungsten oxide at the stage of catalyst preparation. Activity of the catalyst appears to be related to its nonstoichiometric oxidation state. The reduced form of tungsten oxide, formed during metathesis of propene, appears to be stabilised and is at least partly resistant to reoxidation during catalyst regeneration. Catalyst induction appears to be a two-step process involving reduction of the catalyst accompanied by the formation of acetone and possible formation of a metallocarbene

along with acetaldehyde. Activity of the catalyst is affected by conditions of catalyst activation and this may involve a change in the activity per site and the total number of sites as is manifested by a change in the interphase mass transfer behaviour.

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