Skeletal Isomerisation of 1-Butene on Tungsten Oxide Catalysts

L. H. Gielgens, M. G. H. van Kampen, M. M. Broek, R. van Hardeveld, and V. Ponec[1]

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

Several γ-Al_2O_3-supported tungsten oxide catalysts have been studied in the skeletal isomerisation of 1-butene. It appears that the presence of small tungsten oxide particles induces skeletal isomerisation. Large particles can be activated by prereduction treatment with hydrogen. It was shown that the selectivity and stability of the catalysts depend strongly on the tungstate loading. A sudden increase in selectivity is observed when dimeric WO_4^{2-} species are formed. A low density of active sites presents deactivation, which is caused by carbonization of the catalyst due to oligomerisation of isobutene. The main by-products, C_3 and C_5 hydrocarbons, arise from the dimerisation and cracking of isobutene. © 1995 Academic Press, Inc.

INTRODUCTION

Skeletal isomerisation of 1-butene to isobutene is interesting because of its potential practical application, and because of the fundamental problems encountered. The first aspect is related to the new formulations of gasoline and the important additive methyl tertiary-butyl ether (MTBE) which can be easily produced from isobutene and methanol. The attractive fundamental aspect is the very existence of this reaction, since on the basis of the earlier literature one would expect that C_4 hydrocarbons would not isomerise skeletally, although they can undergo scrambling of carbon atoms over the four positions in the linear molecule (1, 2). Contrary to the theoretical prediction, several catalysts have been reported to induce skeletal isomerisation: modified aluminas (3–5), zeolites (6–9), and tungsten oxides (10, 11). The last mentioned of these catalysts was the subject of later studies by others (12) and is the catalyst investigated in the present work.

The inventors of the tungstate catalyst (10, 11) prepared it from $Na_2WO_4 \cdot 2H_2O$, mounted it on α- or γ-alumina, and activated it by acidic extraction of sodium ions (HNO_3) and subsequent reduction by wet hydrogen. It seemed interesting to us to investigate how tungsten oxide prepared in this way differs from other forms of the oxide, since such studies in the literature often appeared to be helpful in the identification of the active sites.

[1] To whom correspondence should be addressed.

METHODS

Catalyst Preparation and Characterisation

Catalysts were prepared by impregnation of a γ-Al_2O_3 support (Akzo Nobel, CK300, 200 m^2/g) with an aqueous solution containing the appropriate amount of the precursor. Two kinds of tungsten oxide catalysts were prepared with a 30 wt% loading of tungsten oxide. One was prepared by impregnation with an ammonium metatungstate precursor ((NH_4)$_2WO_4 \cdot 16H_2O$, Aldrich) while the other was prepared as described by Baker and Clark (10), starting from a sodium tungstate salt ($Na_2WO_4 \cdot 2H_2O$, Merck). After the water evaporated, the catalysts were dried overnight at 120°C and calcined in air at 450°C for 4 h. These catalysts were respectively denoted as W30-NH_4 and W30-Na. After drying, a part of the catalyst W-Na was washed with nitric acid to remove the sodium (catalyst W30-Na-Ac), followed by calcination in air (450°C for 4 h). In experiments to be indicated, this catalyst is reduced before use at 475°C for 4 h by hydrogen (marked as catalyst W30-Na-Ac-H) or by carbon monoxide (catalyst W30-Na-Ac-CO). All the different 30 wt% loaded catalysts are listed in Table 1.

In order to investigate the role of tungsten oxide loading we prepared several WO_3/γ-Al_2O_3 catalysts by impregnating the γ-alumina support with different amounts of ammonium metatungstate. After evaporating the water, the catalysts were dried overnight at 120°C and calcined in air at 450°C for 4 h. We varied the loading between 2 and 30 wt%. Catalysts of this series are indicated by Wx-NH_4, in which x is the loading of tungsten oxide. The catalysts were characterized by X-ray diffraction (XRD), UV–visible spectroscopy (UV/Vis), transmission electron microscopy (TEM), and thermal gravimetric analysis (TGA).

Catalytic Testing

The catalysts were tested in an all-glass continuous flow apparatus. All tests were performed with 0.50 g (powder) catalyst. The standard feed was a mixture of 10 vol% 1-butene in N_2 (total flow: 20 ml/min). The catalyst was tested at 400°C (isothermal) or in a temperature-pro-

TABLE 1

Codes and Preparation Method of the Different 30 wt%
WO$_3$-Loaded Catalysts Tested

Catalyst code	Precursor	Acid treatment[a]	Reduction
W30-NH$_4$	(NH$_4$)$_2$WO$_4$ · 16H$_2$O	No	No
W30-Na	Na$_2$WO$_4$ · 2H$_2$O	No	No
W30-Na-Ac	Na$_2$WO$_4$ · 2H$_2$O	Yes	No
W30-Na-Ac-H	Na$_2$WO$_4$ · 2H$_2$O	Yes	Yes, with H$_2$
W30-Na-Ac-CO	Na$_2$WO$_4$ · 2H$_2$O	Yes	Yes, with CO

[a] Acid treatment as described by Baker and Clark (10).

grammed run (20°C to 400°C, 0.75°C/min). The 1-butene (Hoekloos, 99.0%) and nitrogen (Hoekloos, 99.95%) were used without purification.

Before the test began the catalyst was dehydrated (400°C, 2 h, 20 ml/min N$_2$) or reduced (475°C, 4 h, 20 ml/min H$_2$). The flow was regulated by mass-flow controllers (Bronkhorst Hi-Tec). During some tests the flow was saturated with water vapour at 25°C (P$_{H_2O}$ = 18 Torr). The product stream was analyzed by a gas chromatograph (Chrompack 438a) equipped with a Chrompack capillary column (PLOT fused silica, 50 m, 0.32 mm i.d., Al$_2$O$_3$/KCl coating).

Analysis of mixtures containing in the most general case mono-olefins and alkanes from C$_1$ to C$_8$ in various isomers is not easy. Catalytic behaviour of the catalysts used was, therefore, evaluated in a simple way, just on the basis of the FID signals, I. Conversion is defined in Eq. [1], where $I^{1\text{-butene}}$ stands for the 1-butene signal, and $\sum I^{\text{products}}$ for the summation of all product-signals:

$$\alpha(\%) = 100 \times (I^{1\text{-butene}}/(I^{1\text{-butene}} + \sum I^{\text{products}})). \quad [1]$$

The selectivity to isobutene, for example, is defined in Eq. [2], where "products" indicates that only products of the 1-butene reaction are considered. Since the signal is proportional to the number of carbon atoms, we can speak essentially of wt%. The product $\alpha \times S/100$ is called "yield":

$$S_{\text{iso}}(\text{wt\%}) = 100 \times (I^{\text{iso-butene}}/\sum I^{\text{products}}). \quad [2]$$

The term "initial selectivity" is defined as the selectivity after 30 min on-stream. Selectivity defined as it is in our paper *is* actually a measure of activity for skeletal isomerisation. All other isomerisations are in equilibrium and against this background the relative extent of skeletal isomerisation is also a measure of activity in this reaction.

RESULTS

Catalyst Characterisation

Several catalysts with the nominal loading 30 wt% WO$_3$ have been prepared. Sodium tungstate mounted on γ-Al$_2$O$_3$ is white and by XRD the Na$_2$WO$_4$ phase is seen. Nitric acid treatment turns the colour bright yellow. After calcination the catalyst is pale yellow and XRD reveals the WO$_3$ phase. By a thorough acid treatment sodium can be removed almost quantitatively, as checked with neutron-activated elemental analysis. When γ-Al$_2$O$_3$ is impregnated by (NH$_4$)$_2$WO$_4$ · 16H$_2$O, the colour is white and by XRD no crystalline phase is detected. However, elemental analysis confirms the presence of tungsten on the catalysts. The catalyst W30-Na-Ac contains particles of size 10–15 nm, while only very small particles (<3 nm) can be seen on the catalyst W30-NH$_4$, as determined by TEM and XRD peak-broadening. When the yellow W30-Na-Ac catalyst is reduced at 475°C in hydrogen the colour turns to blue, and after reduction in carbon monoxide it turns to green-yellow.

All the tungsten oxide catalysts with loadings between 2 and 30 wt% prepared by impregnation with ammonium metatungstate were white and no crystalline phase could be detected by XRD. Only the W30-NH$_4$ catalyst was checked by TEM. Visible tungsten oxide particles were almost completely absent. The UV/vis spectra of these catalysts were recorded for catalysts of different loadings, mainly in order to detect the lateral interaction in the tungsten oxide layer. They are displayed in Fig. 1 and one observes there absorption bands attributable to W(VI).

Catalytic Results

Various 30 wt% loaded catalysts show very different catalytic behaviour. The W30-Na catalyst is totally inactive, having also zero activity for the double-bond shift
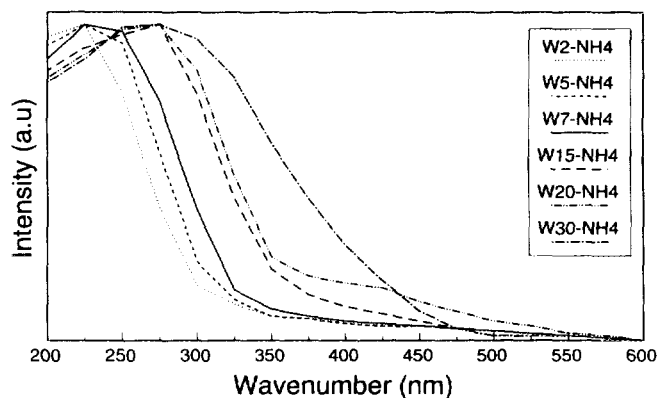

FIG. 1. UV–visible spectra of the catalysts W2-NH$_4$, W5-NH$_4$, W7-NH$_4$, W15-NH$_4$, W20-NH$_4$, and W30-NH$_4$.
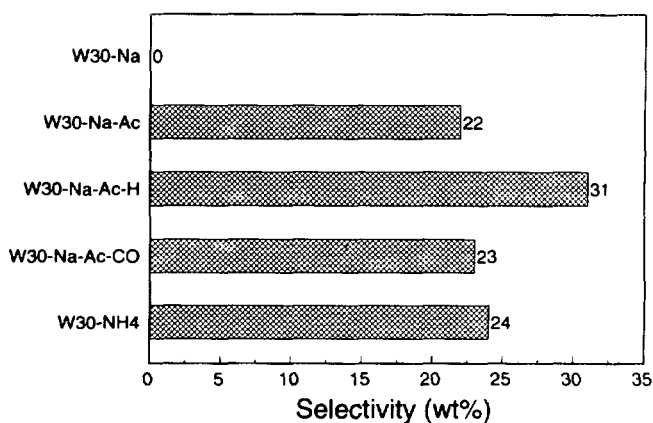
FIG. 2.   Initial selectivity (viz. after 30 min on-stream) to isobutene of all the different 30 wt% loaded catalysts at 400°C. The conversion is in all cases about 80–85%.
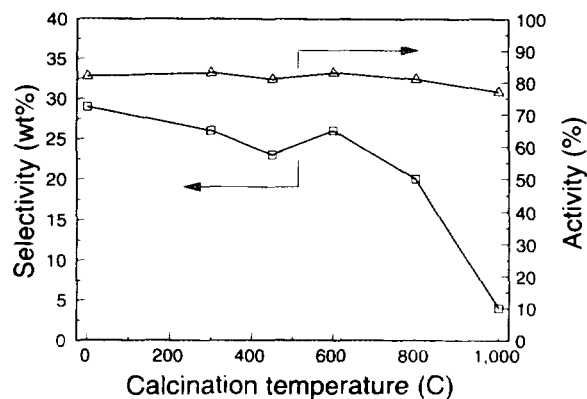

FIG. 3.   Influence of the calcination temperature on the initial selectivity (viz. 30 min on-stream) to isobutene and activity for catalyst W30-NH₄ at 400°C (The catalyst has been calcined at the indicated temperature for 4 h in air). After calcination at 1000°C Al₂(WO₄)₃ is formed, as determined by XRD.

isomerisation. Sodium tungstate actually acts as a poison for the (skeletal) isomerisation activity of the alumina support. When sodium had been extracted, the catalyst (W30-Na-Ac) showed a double bond shift and *cis/trans* isomerisation (we shall call them together a 'linear isomerisation'), and also, in contrast with results presented by Baker and Clark (10), skeletal isomerisation. After a thorough reduction at 475°C (catalyst W30-Na-Ac-H), a small increase in skeletal isomerisation activity was observed. This effect is not seen after reduction with carbon monoxide. The W30-NH₄ catalyst also shows skeletal isomerisation activity without any pretreatment. A comparison of the various catalysts at standard conditions is shown in Fig. 2.

Evolution of different isomerisation activities with increasing temperature of the catalytic reaction demonstrated that the double bond shift isomerisation produces at low temperatures more *cis*-2-butene than *trans*-2-butene. This has been frequently seen in the literature (13, 14) and was also observed with modified (halogenated) aluminas (15). At higher temperatures the *cis/trans* isomerisation brings the linear isomerisation almost to thermodynamic equilibrium, on which the production of isobutene is superimposed.

An attempt has been made here to learn more about the active centres for skeletal isomerisation by monitoring the influence of water vapour and calcination temperature. The surface concentration of the OH groups is assumed to vary both with varying calcination temperature and with the presence or absence of water in the feed.

Fig. 3 shows the initial selectivity to isobutene in the standard catalytic test as a function of the calcination temperature (a catalyst has been kept at the indicated temperature for 4 h, in air) for the W30-NH₄ catalyst. With increasing calcination temperature a small decrease of selectivity is seen, mainly when the calcination temper-

ature exceeds 600°C. The linear isomerisation activity is not affected. After calcination at $T = 1000$°C, formation of Al₂(WO₄)₃ was observed by XRD, and the skeletal isomerisation activity is found to be near to zero.

In some experiments saturated water vapour (18 Torr) was admixed with the standard feed and after a period of time removed from it again. It can be seen in Fig. 4 that water vapour increases the selectivity to isobutene. This effect of H₂O is essentially reversible.

Let us turn our attention to the production of side-products. In the initial stage of a standard catalytic test at 400°C by-products are observed, mainly C_3 and C_5 hydrocarbons, formed in a molar ratio of about 1. Initially, there are about 12–14 wt% by-products. As shown in Fig. 5, the formation of by-products decreases with time. A
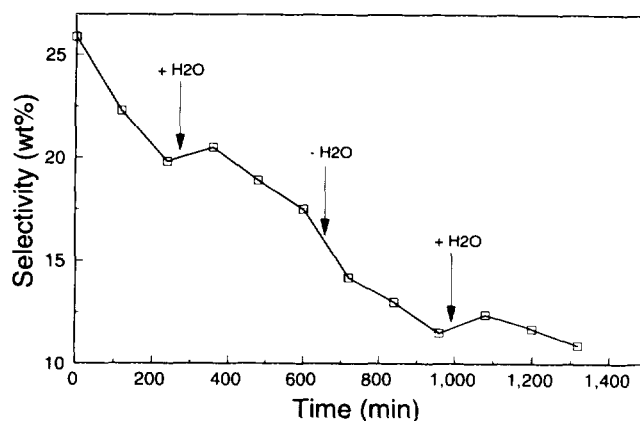

FIG. 4.   Effect of water on the selectivity to isobutene of the catalyst W30-NH₄ ($p_{H_2O} = 18$ Torr). At the points labeled "+H₂O" water was mixed into the feed, at the points labeled "−H₂O" a dry feed was used. The first product analysis was 15 min after changing the feed composition. The effect is superimposed on normally seen deactivation.
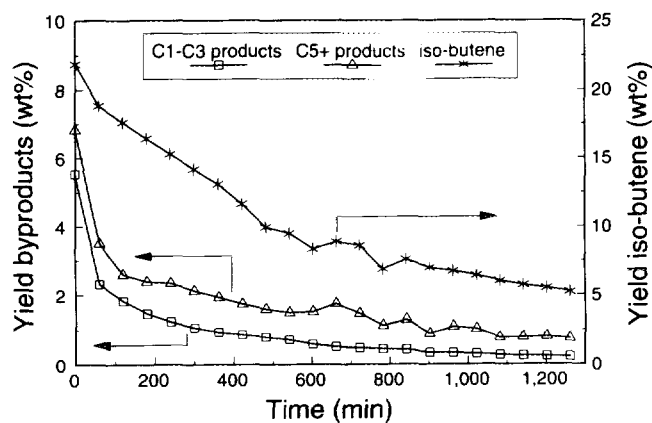
FIG. 5. By-product distribution and yield to isobutene as a function of time-on-stream at 400°C for catalyst W30-NH$_4$. Propene and C$_5$-hydrocarbons are the main by-products.

decrease in skeletal isomerisation activity is also observed. Surprisingly, the linear isomerisation activity is not affected.

Finally, we focus on the influence of the WO$_3$ loading. A remarkable relation between the loading and both the selectivity and the stability of the catalysts was observed. Increasing the tungsten oxide loading results in increasing selectivity to isobutene. It is interesting that there is an increase in the initial selectivity at a loading of about 7 wt% (see Fig. 6).

To check whether the selectivity jump is an effect of a new tungstate structure appearing, the following experiment was performed. In contrast with the experiments described above, the reactor was filled with a fixed amount of tungsten oxide (on a support). As a standard we used 0.5 g of the 5 wt% WO$_3$/γ-Al$_2$O$_3$ (W5-NH$_4$) catalyst and compared it with catalysts of higher loading. The latter catalysts were used in smaller total amounts, so that in

all experiments the same amount of WO$_3$ (on a support) was in the reactor. A catalyst of a higher WO$_3$ content, used in smaller amounts, was always diluted with inert quartz (Merck) in order to produce approximately the same catalyst bed volume. With all catalysts the standard catalytic test at 400°C was performed. In this way several loadings were compared with the standard catalyst and, as demonstrated by Fig. 7, an increase in the selectivity, with a maximum at 15 wt%, is observed. If the catalytic activity per unit weight of WO$_3$ were the same with all the catalysts, the activity of all catalysts used in various amounts should be the same, because the reactor always contained the same amount of WO$_3$. However, we observe a sharp increase up to 15 wt% WO$_3$ which in our opinion indicates that at higher WO$_3$ loadings more of a catalytically active form of WO$_3$/γ-Al$_2$O$_3$ is formed. The decrease at still higher loadings indicates, together with the observations in Fig. 6, that a multilayer of WO$_3$ is formed at high loadings.

As already mentioned, the stability of the catalyst is also surprisingly influenced by the loading. It is obvious from Fig. 8 that only the 7 wt% loaded catalyst does not deactivate with increasing time-on-stream. The high-loaded catalysts have a high initial selectivity but exhibit a strong deactivation. After 16 h on-stream all catalysts with a loading higher than 5 wt% have approximately the same selectivity.

The deactivation of the low-loaded catalysts is remarkable. At low coverages by WO$_3$, one monitors (actually) the activity of γ-Al$_2$O$_3$ and also its self-poisoning. WO$_4^{2-}$ blocks the acidic sites of γ-Al$_2$O$_3$ and from a certain coverage it becomes active itself.

To determine the amount of carbon deposited on the catalysts after 16 h on stream, we made a short study by thermogravimetric analysis (TGA). The deposited carbon
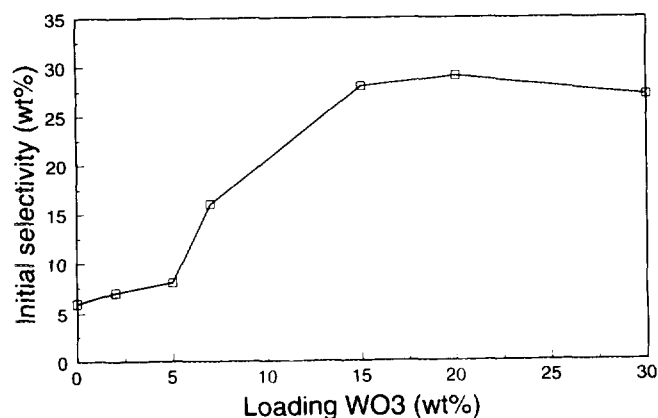

FIG. 6. Influence of the tungstate loading on the initial selectivity (viz. 30 min on-stream), tested with a fixed amount of catalyst (0.50 g).
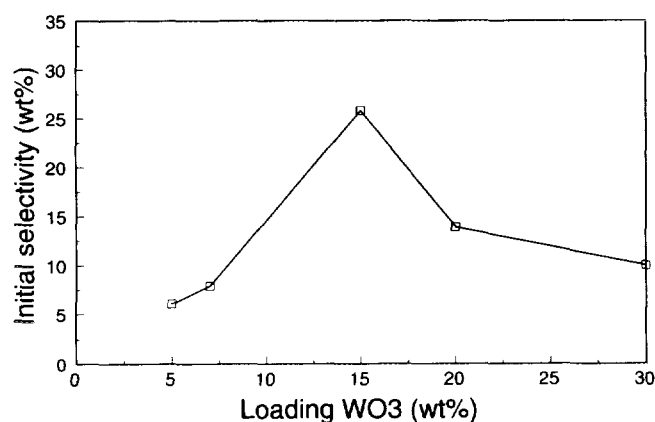

FIG. 7. Influence of the tungstate loading on the initial selectivity (viz. 30 min on-stream), tested with a fixed amount of tungsten oxide (reference catalyst: W5-NH$_4$).
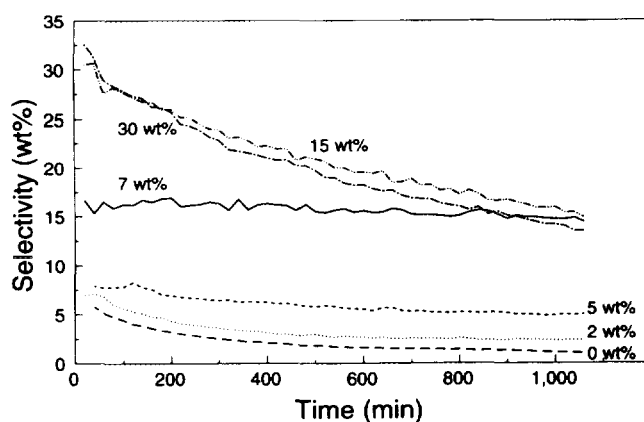
FIG. 8. Stability at 400°C of the catalysts W2-NH₄, W5-NH₄, W7-NH₄, W15-NH₄, and W30-NH₄ during time-on-stream.

was burnt off in a pure oxygen stream, at a temperature increasing up to 600°C. This TGA study shows that the catalysts showing strongest deactivation contain the most carbon. The main part of the deactivation can thus be ascribed to carbonaceous deposits. It should be noted that a small fraction of the weight change is due to reoxidation of tungsten oxide (for high-loaded catalysts, the actual weight loss due to carbon combustion can be 10% higher), but it is mainly the trend in the figure and the comparison of Fig. 9 with Fig. 6 which are essential for the discussion.

DISCUSSION

Catalysts with WO₃ are certainly quite promising for skeletal isomerisation of butene. A recent paper (12) reports 14% isobutene selectivity at 450°C, using a pure n-butene feed, with TiO₂-supported WO₃. Another paper (16) shows a figure of 5%, at 350°C, with unsupported

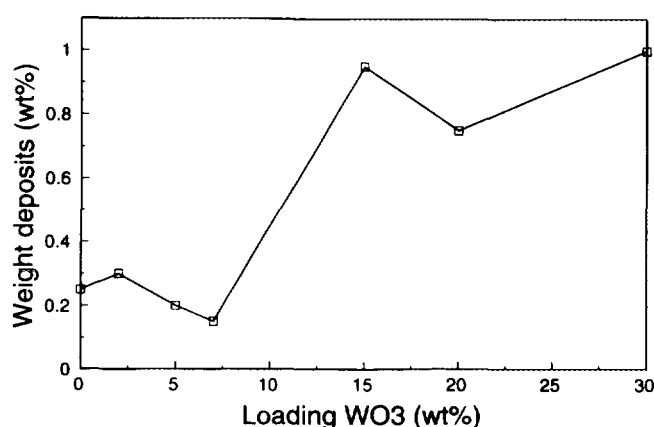FIG. 9. Weight of carbon deposited on various catalysts after 16 h on-stream at 400°, determined by weight loss upon oxidation by TGA measurements.

WO₃. Our results show that 15 wt% isobutene at 400°C is easily achievable in a steady state while initial selectivities up to 30 wt% are possible. There is hope that further work on optimisation would bring about improvement of the catalysts.

In contrast with what is reported by Baker and Clark (10), we found that no prereduction treatment of the catalyst W30-Na-Ac was necessary to induce skeletal isomerisation activity. The contradicting results could arise from differences in tungsten oxide particle size of the catalysts used. Although the catalyst W30-Na-Ac is prepared as described by Baker and Clark (10), differences in tungsten oxide particle size may arise from the alumina support used. Unsupported tungsten oxide, containing large particles, also shows skeletal isomerisation activity only after a reduction at 700°C, but even then the selectivity is below 5% (16). Probably no activation by prereduction is necessary if the catalyst contains small tungsten oxide particles.

The reduction treatment, as reported by Baker and Clark, creates interalia oxygen vacancies in the crystal structure. The individual defects are not stable if the tungsten particles are large, because the large particles have the capability to form shear structures (17–20), and "repair" the defects. If the catalyst is reduced at a sufficiently high temperature, many defects can be created and formation of the shear structures does not deactivate all of them. After the tungsten oxide is mounted on a carrier, a loss of defects due to shear structure formation is probably prevented, and consequently a less severe reduction is sufficient. When the particle size of tungsten oxide is sufficiently low no prereduction is necessary to obtain skeletal isomerisation activity. This is the case with catalysts W30-NH₄ and W30-Na-Ac. The skeletal isomerisation activity of catalyst W30-Na-Ac, with large tungsten oxide particles, can be increased by prereduction treatment. The selectivity of catalyst W30-NH₄ is not influenced by a prereduction step. Another consequence of reduction by hydrogen is the formation of OH groups and, in the bulk of oxides, of tungsten bronzes. This, too, can influence the catalytic properties of WO₃. The latter idea seems to be supported by the observation that activation of WO₃ is not achieved when WO₃ is reduced by carbon monoxide (see Fig. 2).

Changing the population of OH groups on the active surface by varying the calcination temperature (Fig. 3) influences the skeletal isomerisation activity only marginally, whereas adding water to the feed increases the selectivity measurably (Fig. 4). It is possible that newly created OH groups are responsible for the rise in selectivity. However, we also have seen indications that water influences the extent of carbonaceous deposits (21).

Initially, about 12–14 wt% by-products are formed. The main by-products in a standard catalytic test at 400°C are C₃ (mainly propene) and C₅ hydrocarbons. It is possible
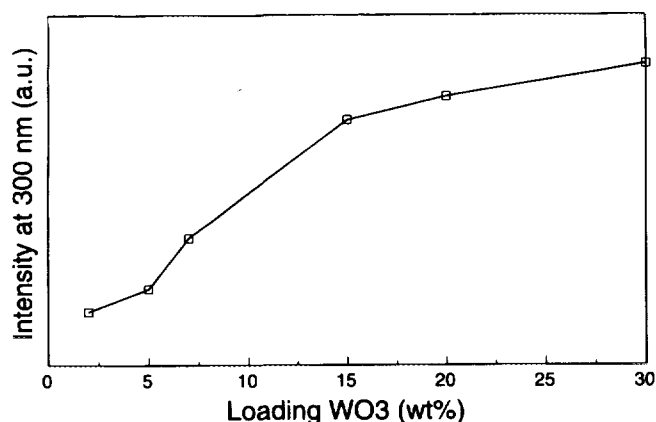
FIG. 10. Intensity of the absorption band at 300 nm as a function of tungsten oxide loading.

that these by-products originate from the cracking of C_8 hydrocarbons, because they are always in a molar ratio of about 1, as shown in Fig. 5. It is remarkable that there are almost no C_2 and C_6 by-products formed. This could indicate that the by-products are formed by the cracking of a trimethylpentene intermediate, produced by dimerisation of two *isobutenes* (22). If, namely, the intermediate were a 3-monomethylheptene or a 3,4-dimethylhexene, from dimerisation of two *n*-butenes (22–25), some C_2/C_6 by-product could also be expected. In the case of 3,4-dimethylhexene formation, a direct cracking to C_3/C_5 molecules is even not possible. With decreasing isobutene formation, a decrease in by-product formation is also observed; this is likely to indicate that isobutene and by-products are formed by a consecutive reaction, most probably on two different sites.

The structure of tungsten oxide on alumina is very well described in the literature (26–32). At a low loading, the tungsten forms mono-WO_4^{2-} species on the surface, but with increasing loading, di- and poly-WO_4^{2-} species are formed. At loadings around a monolayer coverage (above 15 wt%) crystalline species are present. The sharp jump in selectivity at 7 wt% loading is in the region where according to the literature (26–32) the first dimeric WO_4^{2-} species are formed. At 15 wt% we already reach the maximum amount of the "ideal" tungstate species (see Figs. 6 and 7). The UV/vis experiments indicate the same; with increased loading a broadening of the absorption band around 300 nm is observed, and this indicates the subsequent formation of poly-WO_4^{2-} species (33). Figure 10 shows that this broadening of the absorption band around 300 nm is indeed extra strong above 7 wt% loading, and it levels off at loadings higher than 15 wt%.

Consequently, we speculate that the selectivity increase at loadings above the 7 wt% tungsten oxide loading indicates that doublets of active sites are required for the

reaction. There are several potential reasons for this: (i) the required, probably weak, OH group is mainly formed in doublets, triplets, etc.; (ii) a molecule of *n*-butene needs two sites to become activated for skeletal isomerisation, e.g., an oxygen vacancy and an "eligible" OH group in each other's neighbourhood, which are more easily formed or are more active in doublets, triplets, etc., than in isolated WO_4^{2-} species; or (iii) two butenes have to react simultaneously (a bimolecular mechanism). As demonstrated by Fig. 8, a high density of active sites causes severe deactivation due to carbonization of the catalyst. This is probably induced by polymerisation of activated isobutene. With a low density of active sites, the isobutene molecules are possibly so far from each other that no polymerisation, and thus no deactivation, occurs.

CONCLUSIONS

Alumina-supported tungsten oxide catalysts are, after a specified pretreatment or preparation, active in the skeletal isomerisation of 1-butene. A sudden increase in selectivity occurs when dimer WO_4^{2-} species at the catalyst's surface become abundant, indicating that (i) the active site is only formed in dimer WO_4^{2-} species, (ii) two active sites acting simultaneously are needed, or (iii) two *n*-butenes react simultaneously. If there is a high density of active sites, deactivation occurs due to carbon deposition, apparently due to polymerisation of isobutene. Wetting the feed has a positive influence on the selectivity.

The main by-products are C_3 and C_5 hydrocarbons, produced in a molar ratio of about unity, while almost no C_2 and C_6 by-products are formed. This could indicate that the by-products originate from cracking of a trimethylpentene intermediate, which in its turn is produced from the desired product, namely isobutene. Skeletal isomerisation activity can easily be suppressed, while linear isomerisation activity is maintained. Apparently, skeletal isomerisation requires a different active site from that of linear isomerisation.

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