

IR Spectroscopic Study of the Skeletal Isomerisation of Butene by Alumina-Supported Tungsten Oxide Catalysts

S. Meijers, L. H. Gielgens, and V. Ponec¹

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

Received January 13, 1995; accepted May 12, 1995

The surface properties of supported tungsten oxide catalysts, pure tungsten oxide, and pure alumina were studied by IR spectroscopy, using pyridine and carbon monoxide as probes. The interaction of these catalysts with *n*-butenes, molecules which are isomerised selectively by the catalysts to isobutene, has also been studied by IR spectroscopy. A correlation is found between the catalytic properties of the catalysts and the strength and nature of the acidic sites found on their surface. © 1995 Academic Press, Inc.

INTRODUCTION

In the last five decades much research has been carried out on the selective isomerisation of *n*-butenes to isobutene. Isobutene is used in the synthesis of methyl-*tert*-butyl-ether (MTBE), a well-known nonaromatic octane number booster, which has the additional advantage of containing an internal oxygen atom, reducing the amount of CO formed during fuel combustion.

The skeletal isomerisation of butene is also of theoretical interest. It was thought for a long period that skeletal isomerisation is not possible with hydrocarbons containing four carbon atoms (1). However, skeletal isomerisation activity is found with butenes for a wide range of completely different catalysts, namely, supported metal oxides (2–4), modified oxides (5–8), and zeolites (9–11). It is not known whether the action of these catalysts has anything in common, partly because the mechanism of the isomerisation is still being discussed.

A skeletal rearrangement in a classical carbenium ion has very often been proposed in the literature as the mechanism responsible for skeletal isomerisation (6, 12–14). However, this would involve the formation of a primary carbenium ion following the CH₃ shift, which is unlikely. The *cis/trans* isomerisation and double bond shift of *n*-butenes have been explained by many authors by operation of a π -allylic intermediate. This kind of surface com-

pound has been observed using UV spectroscopy (15) and IR spectroscopy (16, 17). A π -allyl species is also a reasonable candidate for the intermediate in the skeletal isomerisation, since it has been shown by quantum chemical calculations that a π -allylic cation can rearrange via a cyclic transition state. Breaking of the appropriate bond in the cyclic moiety formed from *n*-butene should yield isobutene (18).

Another possible intermediate for the skeletal isomerisation was suggested by Kazansky and Senchenya (19, 20). Many alkenes react, upon adsorption on oxides, with surface hydroxyl groups to surface alkoxy compounds. The C–O bond in these stable surface species is covalent, but in the excited state the C–O bond is stretched and becomes more ionic, with positive charge on the C atom. Thus, a short-living, carbenium ion-like species in which rearrangement might occur can be easily formed from a stable and abundant surface compound. This makes the surface alkoxy group an attractive candidate for the intermediate in butene skeletal isomerisation. Moreover, the required excitation of an alkoxy group has possibly a lower activation energy than the direct formation of a classical carbenium ion from an alkene (20). In zeolites, the existence of activated surface alkoxy groups has been proven by NMR spectroscopy (21).

Finally, a bimolecular mechanism has been suggested by Szabo *et al.* (14) for the skeletal isomerisation of butene in the zeolite ferrierite. Rearrangement of butene dimers (octenes) to branched octenes via a carbenium ion intermediate does not require a primary carbenium ion as in the case of butene. After rearrangement, the dimers are cracked to form two C₄ alkenes, at least one of which is isobutene. The specific environment provided by the zeolite matrix is supposed to stimulate this mechanism.

For this study, a series of alumina-supported tungsten oxide catalysts was studied using FTIR and DRIFT spectroscopy. This series has been chosen since it allows the comparison between catalysts with different catalytic activity and selectivity, but similar loading and specific surface area, and which are prepared from the same starting mate-

¹ To whom correspondence should be addressed.

rial. Some of the supported tungsten oxides are very active and selective in the transformation of *n*-butene to isobutene and their catalytic properties and other characteristics are well known (22). In this study, pyridine and CO adsorption were used to characterise the surface of the catalysts. The adsorption modes of different butenes were studied and a comparison is made between several active and inactive supported tungsten oxides, the pure carrier (γ -alumina) and pure WO_3 .

METHODS

Supported tungsten oxide samples were prepared by impregnation of $\gamma\text{-Al}_2\text{O}_3$ (Akzo CK300) with aqueous solutions of $(\text{NH}_4)_2\text{WO}_4 \cdot 16\text{H}_2\text{O}$ (Aldrich) and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (Merck). The concentration of the solutions was chosen in such a way that a load of 30 wt.% of WO_3 on alumina would be obtained. With this loading the alumina is covered with one monolayer of tungsten oxide (22).

The catalyst prepared from ammonium tungstate, which will be referred to in this paper as W-NH_4 , was catalytically active and selective as such. Analysis of the IR spectrum excluded the presence of NO_x on the surface of this catalyst. Poisoning of the catalyst by 1 wt.% Na was achieved by postimpregnation with a solution of Na_2CO_3 and calcination of the sample for 8 h at 400°C . This poisoned W-NH_4 will be denoted as 1 wt.% Na/ W-NH_4 . The catalyst prepared from sodium tungstate (W-Na) has been activated as described by Baker *et al.* (23, 24): the procedure was a first washing with nitric acid, after which the sample denoted as W-Na-Ac , then a reduction in a flow of hydrogen, producing a sample denoted as W-Na-Ac-H . The pure WO_3 studied was from Fluka A. G. Neutron activation analysis was used to check for the presence of any Na left in W-Na-Ac after the acid treatment. The amount of Na left was 60 mg per kg of catalyst. A more detailed description of the preparation method and characteristics of the catalyst can be found in Ref. (22). The catalytic activity of the samples was tested in a flow system with a fixed bed reactor. Analysis of the products was made by gas chromatography (22). Table 1 gives the catalytic properties at 350°C of the samples used in this study. On pure alumina and on the supported tungsten oxides the relative amounts of the *n*-butenes were mutually in thermodynamic equilibrium.

For the IR spectroscopic measurements pellets with a diameter of 2.8 cm were made of about 50 mg of each sample using a pressure of 1×10^7 Pa. The pellets were placed in an infrared transmission cell equipped with CaF_2 windows and connected to a conventional gas manipulation and evacuation system. Spectra were recorded with a resolution of 2 cm^{-1} between 2400 and 1200 cm^{-1} by a Mattson Galaxy 3000 FTIR spectrometer. The samples were activated by outgassing in vacuum at 350°C . Due to insufficient

TABLE 1
Catalytic Properties in the Isomerisation of Butene of Al_2O_3 , WO_3 , and Alumina-Supported Tungsten Oxides

Sample	Specific surface area (m^2/g)	Conversion (%)	<i>S</i> isobutene ^a (wt.%)
Al_2O_3	200	80	5
WO_3	10	~0	0
W-Na	~100	0	0
W-Na-Ac	~100	80	22
W-Na-Ac-H	~100	80	31
W-NH_4	~100	80	24
1 wt.% Na/ W-NH_4	~100	65	0

^a $S_{\text{ISO}} = 100 \times (I^{\text{ISO}} / \sum I^{\text{products}})$, where *I* stands for FID signal (22).

transparency of the supported tungsten oxides in the C-H stretching region, this part of the spectra of adsorbed butenes was not available for interpretation. Adsorption of the butenes (Messer Griesheim), 2-butanol (J. T. Baker B. V.), and pyridine (Aldrich) was carried out at room temperature. Carbon monoxide (Messer Griesheim) was adsorbed at -150°C .

Since the supported tungsten oxide prepared from sodium tungstate was not transparent after reduction, this sample was studied using diffuse reflectance (DRIFT) spectroscopy. In this case, the measurements were carried out in a flow system with Ar as carrier gas. The cell used was a Spectratech environmental DRIFT cell and spectra were recorded by a Perkin-Elmer 1760 X spectrometer.

RESULTS

Characterization by Pyridine Adsorption

The spectra of pyridine adsorbed on supported tungsten oxides, γ -alumina, and pure tungsten oxide were recorded between 1700 and 1400 cm^{-1} and assigned according to Parry (25) and Boehm and Knözinger (26). The results are summarised in Table 2.

The spectrum of pyridine adsorbed on pure alumina shows after evacuation of the sample at room temperature bands that can be assigned to hydrogen-bonded pyridine, coordinatively bonded pyridine, and a very small amount of pyridinium ions. The pyridinium ion is not frequently found on pure Al_2O_3 . Its presence or absence is a question of the type of alumina used. Evacuation at 100°C has no influence on the intensities of the bands arising from coordinatively bonded pyridine and the pyridinium ion. In contrast, the spectrum of hydrogen-bonded pyridine decreases considerably in intensity.

Pyridine adsorption on pure WO_3 produced bands assignable mainly to coordinatively bonded pyridine and a very small amount of hydrogen-bonded pyridine. The pyri-

TABLE 2
Bands (Wavenumber Values in cm^{-1}) Observed in the IR Spectra of Pyridine Adsorbed on Al_2O_3 , WO_3 , and Alumina-Supported Tungsten Oxides and Their Assignments (25)

Al_2O_3	WO_3	W-Na-Ac	W-Na-Ac-H	W-NH ₄	1 wt.% Na/W-NH ₄	Assignment
			1640 s	1639 w	1636 w	PI
				1622 sh		PI
1612 s	1608 s	1616 m	1615 m	1613 s	1614 s	CB
1592 s		1592 s	1597 s	1599 sh	1594 m	HB
1577 m	1578 m	1577 m	1582 s	1577 m	1577 w	CB
1525 w		1540 w	1546 m,	1543 m	1540 m,	PI
			1537 m		1535 m	
1490 m	1489 m	1490	1491	1490 s	1489 s	CB, PI
	1482 sh		1482			HB
1440 sh	1444 s	1449	1447	1447 vs	1449 vs	CB
1450 vs	1438 sh		1440		1442 sh	HB

Note. HB, hydrogen-bonded pyridine; CB, coordinatively bonded pyridine; PI, pyridinium ion. W-Na is not included here since no adsorption of pyridine was detected on this sample.

dinium ion was not observed. The bands were very weak in comparison to pyridine adsorbed on alumina and disappeared upon heating in vacuum.

On W-Na no adsorption of pyridine is observed, which means that no acidic sites of any type are detectable on the surface of this sample. The spectrum of pyridine adsorbed on the same sample treated with nitric acid, W-Na-Ac, shows bands arising from coordinatively and hydrogen-bonded pyridine and a small amount of pyridinium ions. After the second activation step, i.e., reduction with H_2 , the sample W-Na-Ac-H is dark blue and nontransparent for IR radiation and can be studied only by DRIFT spectroscopy. Adsorption of pyridine followed by outgassing at room temperature produced a spectrum that shows again bands of hydrogen-bonded and coordinatively bonded pyridine, but in comparison with W-Na-Ac the band due to the pyridinium ion has a much higher intensity and is split into two components, with maxima at 1546 and 1537 cm^{-1} . Also a weaker band at 1640 cm^{-1} arising from the pyridinium ion is now visible. Heating of both W-Na-Ac and W-Na-Ac-H leads to a decrease in hydrogen-bonded pyridine and a small increase in the amount of coordinatively bonded pyridine, the latter probably due to the readsorbing of some pyridine, released from weakly bonding sites, on Lewis acidic sites.

Pyridine adsorbed on the W-NH₄ sample showed the same spectrum as pyridine on W-Na-Ac-H: at room temperature the hydrogen-bonded molecule, the coordinatively bonded molecule, and a considerable amount of the cation. After heating in vacuum only the cation and the coordinatively bonded pyridine remain. If this catalyst is poisoned with 1 wt.% Na, the bands of coordinatively bonded pyridine are weaker than on the other supported tungsten oxides. Hydrogen-bonded pyridine and pyridin-

ium ion are found in the same amounts as on W-NH₄ and W-Na-Ac-H. As on the latter sample, the main band of the pyridinium ion is split into two components, with maxima at 1540 and 1535 cm^{-1} .

Characterisation by Carbon Monoxide Adsorption

On pure WO_3 the adsorption of CO at -150°C gives rise to a band at 2193 cm^{-1} . On W-Na the CO stretching band is found at 2167 cm^{-1} . After washing with nitric acid the stretching band of CO adsorbed subsequently on W-Na-Ac is found at 2206 cm^{-1} . Also on the samples W-Na-Ac-H and W-NH₄ the spectrum of adsorbed CO consists of a single band at 2206 cm^{-1} . CO adsorption on the poisoned catalyst 1 wt.% Na/W-NH₄ produces one band at 2167 cm^{-1} , as on the W-Na sample.

Adsorption of Butenes

On alumina, pure WO_3 and W-Na no adsorbed butene was seen in the IR spectra. The spectrum of 1-butene adsorbed on W-Na-Ac is shown in Fig. 1a. A strong band at 1632 cm^{-1} shows that butene is predominantly adsorbed molecularly via π -bonding of the C=C bond (in the gas phase this band is found at 1646 cm^{-1}). A shoulder at about 1653 cm^{-1} arises probably from π -bonded *cis*- and *trans*-2-butene (gas phase: 1667 and 1682 cm^{-1}). Bands at 1463 and 1380 cm^{-1} arise from the symmetric and antisymmetric deformations of methyl groups. The $-\text{CH}_2-$ deformation, the vinylic $=\text{CH}_2$ deformation and the $-\text{CH}_2-$ wagging of 1-butene are found at 1444, 1421, and 1345 cm^{-1} , respectively. Very weak bands at 1606, 1583, and 1550 cm^{-1} are probably due to some oxidation of butene by the IR beam-irradiated sample, leading to the formation of carbonates or carboxylates.

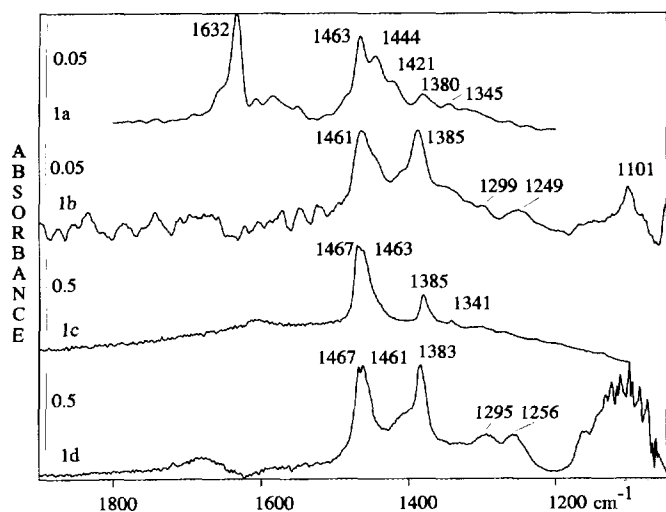


FIG. 1. 1-Butene adsorbed on (a) W-Na-Ac and (b) W-NH₄. (c) 2-Butene and (d) 2-butanol adsorbed on W-NH₄. All spectra were recorded at room temperature and 10⁻⁴ Torr.

Adsorption of 1-butene on W-NH₄, a selective skeletal isomerisation catalyst, leads to a completely different spectrum (Fig. 1b). There is *no* band visible any more in the C=C stretching region. A broad band at 1461 cm⁻¹ with a shoulder at about 1445 cm⁻¹ and bands at 1385 and 1101 cm⁻¹ are very similar to bands observed by others after adsorption of *n*-butenes on different oxides (27) and assigned to the methyl and methylene deformations and the C-O stretching of a secondary surface butoxide. The spectrum is similar to that of 2-butene adsorbed on the same catalyst and identical to the spectrum of 2-butanol adsorbed on this sample, including two weak bands at 1299 and 1249 cm⁻¹. Possibly a small amount of butanol is formed next to the main product, the alkoxy. Butanol cannot be the main product of butene adsorption on W-NH₄, since it is not observed by gas chromatography in the catalytic isomerisation of butene in continuous flow (22).

Adsorption of 2-butene (Fig. 1c) on the same catalyst produced a slightly different spectrum from that of 1-butene adsorption. The intensity of the product bands is higher, which indicates that at ambient temperature 2-butene is more reactive than 1-butene on this catalyst. Further, the intensity ratio between $\delta_{as}CH_3$ and δ_sCH_3 is different. Two additional spectral features are visible in the spectrum. First, there is a splitting of $\delta_{as}CH_3$ into two components at 1467 and 1463 cm⁻¹, which is identical to the pattern observed after adsorption of 2-butanol (Fig. 1d). Second, a weak band occurs at 1341 cm⁻¹, probably due to a -CH- deformation. Bands found in the spectrum of butanol near 1250 and 1300 cm⁻¹ are not detected here. Probably the spectrum of chemisorbed 2-butene consists

of bands partly from the butoxide and partly from the alkoxy of a (branched) polymer, since the C=C double band is absent, but a C-O stretching is not observed either. A polymer alkoxy could account both for the high intensity of δCH_3 and for the lack of observation of $\nu C-O$, since the number of C-O bands would be small compared to the number of C-H bands, while the C-O stretching band has already less intensity than the CH₃ stretching bands in the IR spectra of alkoxy.

The spectrum of isobutene adsorbed at room temperature on W-NH₄ is shown in Fig. 2. At 1153 cm⁻¹ a C-O stretching band indicates that also isobutene reacts to an alkoxy on this catalyst. This spectrum coincides partly with the one observed by Ledo *et al.* (28) after adsorption of isobutene on vanadia-titania: bands at 1479 and 1470 cm⁻¹ from $\delta_{as}CH_3$, at 1393 and 1367 from δ_sCH_3 , and at 1235 and 1202 cm⁻¹ from C-C stretchings. However, some of the bands observed can be assigned neither to isobutene nor to *tert*-butoxide. A small but sharp band at 1336 cm⁻¹ and two weaker bands at 1320 and 1284 cm⁻¹ arise probably from alkane -CH₂- wagging (1336 and 1320 cm⁻¹) and from a -CH= deformation (1284 cm⁻¹). A C=C stretching band at 1630 cm⁻¹ might be assigned to molecular isobutene, but it seems more likely that this band, together with the bands at 1336, 1320, and 1284 arises from an isobutene dimer. Dimerisation of isobutene on isomerisation catalysts has been observed before by IR spectroscopy (29) and it is known also from catalytic activity measurements that isobutene dimerises easily on oxidic catalysts, especially at temperatures below 150°C (30).

On the other selective skeletal isomerisation catalyst, W-Na-Ac-H, the adsorption of butene had to be studied by DRIFT spectroscopy since this catalyst was not transparent for IR radiation. In contrast to the absorption spectra of W-NH₄, W-Na, and W-Na-Ac, the DRIFT spectra

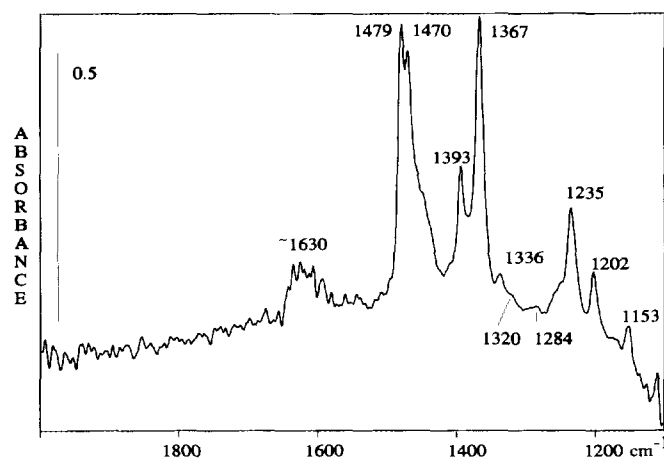


FIG. 2. Isobutene adsorbed at room temperature and 10⁻⁴ Torr on W-NH₄.

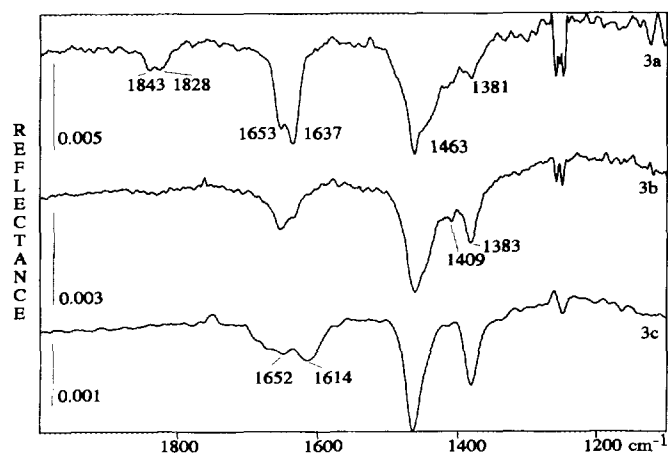


FIG. 3. 1-Butene adsorbed on W-Na-Ac-H. Spectra were recorded at ambient pressure in a flow of Ar at (a) room temperature, (b) 50°C, and (c) 100°C.

of W-Na-Ac-H showed some very weak bands arising from the overtones of W-O and W=O stretching vibrations of tungsten oxide at 2025, 1611, 1456, and 1380 cm^{-1} . The assignment of these bands is disputed (31), but from their weakness it can be concluded that most of the tungsten species is present as a monolayer and very little of it as bulk material.

The behaviour of butene on W-Na-Ac-H is similar to that on W-NH₄. However, at room temperature butene is initially adsorbed molecularly and then slowly converted to a surface alkoxy under heating, whereas on W-NH₄ the alkoxy is observed exclusively. This difference might be explained by the different circumstances under which the two catalysts were studied, namely, W-NH₄ under static conditions in vacuum and W-Na-Ac-H under atmospheric pressure in a flow system. The spectra of 1-butene adsorbed on W-Na-Ac-H are shown in Fig. 3. The band near 1250 cm^{-1} is an artefact of the instrument and not an IR band of an adsorbed species. The spectral features are less well resolved than in the transmission spectra since the reflectivity of the sample is low. In the first minute the spectrum consists mainly of butene bands. Methyl deformations are found at 1463 and 1381 cm^{-1} , the former having a broad shoulder around 1450 cm^{-1} due to the 1-butene -CH₂- deformation. The C=C band is split into two components, one at 1637 cm^{-1} arising from 1-butene and one at 1653 cm^{-1} from 2-butene. The overtones of the vinylic out-of-plane deformation modes at 1843 and 1828 cm^{-1} which were absent in the transmission spectrum are visible in DRIFTS. Heating of the sample to 50°C in a flow of Ar leads to the relative decrease of the 1637 cm^{-1} component of the C=C stretching band, the disappearance of the vinylic bands around 1830 cm^{-1} , and the growth of the symmetric CH₃ at 1383 cm^{-1} . These changes can be explained by the growth of a surface butoxy group. At 100°C

the overall spectrum is very similar to that of 1-butene adsorbed on W-NH₄. Next to the spectral features assigned to the alkoxy a broad weak doublet is visible in the C=C stretching region. This doublet arises probably from some oligomerisation of 1-butene, which was not observed under static conditions in vacuum, but which is well known to happen under a higher pressure in a flow system (22). Unfortunately, C-O stretching bands could not be detected due to a high level of noise in the relevant part of the DRIFT spectrum.

Adsorption of butene on the poisoned isomerisation catalyst 1 wt.% Na/W-NH₄ is very weak. As with W-Na-Ac, all the bands visible in this spectrum can be assigned to molecularly adsorbed butene. Formation of a surface alkoxy group is not observed.

DISCUSSION

Pyridine can be adsorbed on oxides in three different ways, depending on the nature of the acidic sites present on the surface: these are coordinatively bonded to Lewis acidic sites (metal ions), hydrogen bonded to Brønsted acidic hydroxyl groups, which we will call A sites in this paper, and as a pyridinium ion after interaction with another type of, probably stronger, Brønsted acidic hydroxyl groups, which we will call B sites. Upon heating and evacuation of the oxide the pyridinium ion and the coordinatively bonded pyridine usually remain on the surface, whereas the hydrogen-bonded pyridine is desorbed. This behaviour is found with all oxides discussed.

On the two most selective skeletal isomerisation catalysts studied by us, W-Na-Ac-H and W-NH₄, all types of adsorbed pyridine are found, including a considerable amount of pyridinium ion. On W-Na-Ac, which is also selective to isobutene (but less than W-Na-Ac-H), the number of Lewis acidic and A sites is the same, but the number of B sites is lower than that on the two more selective catalysts. On pure alumina, which has a selectivity to isobutene of about 5%, pyridine is mainly adsorbed on Lewis acidic sites, although a small amount of pyridinium ion is observed, too. Pyridinium ion is absent on WO₃ and on W-Na, which are both completely inactive in the isomerisation of butene. Poisoning of W-NH₄ by 1 wt.% Na does not reduce detectably the amount of pyridinium ion formed, in comparison with pure W-NH₄. On 1 wt.% Na/W-NH₄ and on W-Na-Ac-H the strongest band due to the pyridinium ion (near 1540 cm^{-1}) was split into two subbands. This suggests the formation of the ion on two types of Brønsted acidic sites.

Lewis acidity is found on all samples except on supported sodium tungstate (W-Na), which in fact cannot be considered as a butene isomerisation catalyst. On the supported tungsten oxides the Lewis acidic sites are more abundant and stronger than on pure Al₂O₃ or on support-free WO₃.

Carbon monoxide is a sensitive probe for different types of Lewis acidic metal ions in the oxide surface. Carbon monoxide adsorbed on pure tungsten oxide causes an IR adsorption band at 2193 cm^{-1} . Yan *et al.* (31) assigned a band at 2198 cm^{-1} in the spectrum of CO on reduced alumina-supported WO_3 to W^{5+} . Two bands found by these authors at lower wavenumbers and assigned to W^{4+} in different coordinations have not been observed by us. On the supported tungsten oxides W-NH_4 , W-Na-Ac , and W-Na-Ac-H the adsorption of CO gives rise to a single IR band at 2206 cm^{-1} . This wavenumber is too low to assign the band to CO adsorbed on W^{6+} ions (32). It is most likely that it belongs to CO adsorbed on W^{5+} in a lower coordination than the W^{5+} found in pure WO_3 . This idea is supported by our observation in earlier work that the most selective isomerisation catalysts contain very small tungsten oxide particles ($<20\text{ \AA}$), which are expected to have more edges and therefore more coordinatively unsaturated surface ions than pure WO_3 (22). Semiempirical predictions according to Zaki and Knözinger (32) that consider the coordination number and valency of metal ions reveal that bands at 2193 and 2206 cm^{-1} can reasonably well be assigned to CO adsorbed by W^{5+} in fivefold and fourfold coordination, respectively.

The adsorption of CO on W-Na and on the poisoned catalyst $1\text{ wt.}\% \text{ Na/W-NH}_4$ gives rise in both cases to a single IR band at 2167 cm^{-1} . This band can be assigned to CO adsorbed in the neighbourhood of Na^+ ions or on them. For W-Na this is not surprising, since Na_2WO_4 is an inverse spinel compound with Na^+ octahedrally surrounded by oxygen ions. Many spinel compounds expose at their surface mainly $\{110\}$ and $\{100\}$ planes containing only those cations that are octahedrally surrounded in the bulk (33–35). On the surface of the $1\text{ wt.}\% \text{ Na/W-NH}_4$ sample a sodium tungstate phase is probably created by calcination of the impregnated catalyst. The Lewis acidic sites observed by pyridine adsorption on this sample are probably Al ions in the uncovered carrier material, since the tungstate is present as microcrystals (22).

Combining all information on acidic sites obtained by pyridine and CO adsorption with the results of butene adsorption, we arrive at the following conclusion: adsorption of butene is observed only on supported tungsten oxides which have W^{5+} ions in fourfold coordination at the surface. On W-Na-Ac butene is adsorbed mainly molecularly; the shift of the $\text{C}=\text{C}$ stretching band to lower wavenumber shows that butene is π -bonded by a metal ion. On W-NH_4 and W-Na-Ac-H a butoxide is formed. On alumina, pure WO_3 and the sodium-containing samples, butene is only weakly (or not at all) adsorbed. Further, pyridine is protonated to the pyridinium ion on all catalysts which have the ability to transform *n*-butene to isobutene, including the less selective W-Na-Ac and Al_2O_3 . Thus, it seems that the presence of B sites is the most important

(but not the only) condition for butene skeletal isomerisation activity. However, almost equally important seems to be the presence of W^{5+} ions in fourfold coordination, which enhance as Lewis acidic sites the adsorption of butene on the surface. This is illustrated by $1\text{ wt.}\% \text{ Na/W-NH}_4$, which has the same amount of B sites as W-NH_4 but whose activity is greatly reduced due to blocking of the surface by Na^+ . On the other hand, W-Na-Ac has W^{5+} ions in fourfold coordination, but due to its low number of B sites, only a low selectivity towards isobutene. In the two-step activation of W-Na , the role of the treatment with nitric acid is the transformation of supported sodium tungstate into supported tungsten oxide, which has strong Lewis acidic W^{5+} at the surface. The role of the reduction by hydrogen is the creation of B sites rather than the reduction of W ions in the surface. This idea is supported by the facts that the reduction of W-Na-Ac by CO does not increase the activity or selectivity (22) and that the same type of W^{5+} ions are found in W-Na-Ac-H as in W-Na-Ac . The catalyst W-NH_4 is active and selective without pretreatment. This can be explained by the absence in the precursor (ammonium tungstate) of metallic elements other than W which might block W ions and by the possibility that B sites are created during the decomposition of ammonium tungstate. Thus, both conditions for skeletal isomerisation activity are fulfilled.

It is not possible to say whether the surface alkoxy which is formed upon adsorption of butene on the selective skeletal isomerisation catalysts W-NH_4 and W-Na-Ac-H is also the intermediate in the formation of isobutene. Undoubtedly, B sites are necessary, and these groups have the ability to react with butene to surface butoxyl groups. However, it was shown by catalytic activity measurements that the activity and selectivity to isobutene of supported tungsten oxides decrease slowly during the experiment. Obviously there is some poisoning of the active sites, and the poison, or a precursor of it, might be the surface alkoxy. Nevertheless, the idea of a surface alkoxy as the intermediate in the skeletal isomerisation is tempting, since it is observed on the active catalysts in considerable amounts while it is absent on the others.

Although it was found that all *n*-butenes give the same product distribution after reaction over W-NH_4 or W-Na-Ac-H , the reactivity at room temperature of 2-butene on W-NH_4 seems to be higher than that of 1-butene. However, this probably plays no role at 350°C , the working temperature of the catalyst. Even more reactive than 2-butene is the branched butene isomer. In contrast to the *n*-butenes, isobutene adsorbed on W-NH_4 gives detectable dimerisation immediately, beside the formation of *tert*-butoxide. Thus, dimerisation is expected to be a secondary reaction of *n*-butene skeletal isomerisation. This suggests that the main pathway of isobutene formation is monomolecular, rather than a dimerisation-cracking mechanism,

which must be suspected for producing various by-products. Possibly oligomerisation is the first step to catalyst deactivation.

CONCLUSIONS

A strong correlation is found between isomerisation activity and selectivity and the types of surface acidity identified by pyridine and CO adsorption on supported tungsten oxide catalysts. Selective catalysts have Lewis acidic W^{5+} ions in fourfold coordination as well as B-site -OH groups. Lewis acidic sites play a role in the chemical adsorption of butene on the catalyst surface. B sites play a role in the skeletal isomerisation step itself, although it is not clear in which manner. *n*-Butenes react with B sites to secondary surface butoxyl groups, observed on all active and selective catalysts, and butoxyl groups might be the intermediate in the skeletal isomerisation of butene. Next to the butoxide, also some bands assignable to butanol, dimers, and alkoxyls of dimers are detected.

On a catalyst possessing W^{5+} in fourfold coordination but having no B sites, butene was adsorbed as a π -complex and partly isomerised to 2-butene. Sodium-containing samples have no tungsten ions exposed on the surface. These samples are not active in the isomerisation of butene since they cannot bind the olefin effectively to the catalyst.

Isobutene dimerises easily on supported tungsten oxide catalysts. It seems likely that on supported tungsten oxides octenes are a secondary product of butene isomerisation and that most isobutene is formed via a monomolecular mechanism.

Evidence for other possible intermediates in the isomerisation of butene, such as π -allylic species, was not found in our IR spectra.

ACKNOWLEDGMENTS

We thank Dr. R. Ferwerda and Prof. Dr. J. H. van der Maas from the Dept. of Analytical Molecular Spectroscopy, Utrecht University, for the use of their DRIFTS equipment.

REFERENCES

- Brouwer, D. M., and Oelderik, J. M., *Rec. Trav. Chim. Pays-Bas* **87**, 721 (1968).
- Cheng, Z. X., and Ponec, V., *Catal. Lett.* **25**, 337 (1994).
- Patrono, P., La Ginestra, A., Ramis, G., and Busca, G., *Appl. Catal. A* **107**, 249 (1994).
- Yamaguchi, T., Tanaka, Y., and Tanabe, K., *J. Catal.* **65**, 442 (1980).
- Stöcker, M., Riis, T., and Hagen, H., *Acta Chem. Scand. B* **40**, 200 (1986).
- Basini, L., Aragno, A., and Raffaelli, A., *J. Phys. Chem.* **95**, 211 (1991).
- La Ginestra, A., Patrono, P., Berardelli, M. L., Galli, P., Ferragina, C., and Massucci, M. A., *J. Catal.* **103**, 346 (1987).
- Cheng, Z. X., and Ponec, V., *J. Catal.* **148**, 607 (1994).
- Simon, M. W., Suib, S. L., and O'Young, C., *J. Catal.* **147**, 484 (1994).
- Mooiweer, H. H., de Jong, K. P., Kraushaar-Czarnetzki, B., Stork, W. H. J., Krutzen, B. C. H., in "Zeolites and Related Microporous Materials: State of the Art 1994" (J. Weitkamp, H. G. Karge, H. Pfeifer, and W. Hölderich, Eds.), p. 2327, Studies in Surfactant Science and Catalysis, Vol. **84**, Elsevier, Amsterdam, 1994.
- Yang, S. M., Guo, D. H., Lin, J. S., and Wang, G. T., in "Zeolites and Related Microporous Materials: State of the Art 1994" (J. Weitkamp, H. G. Karge, H. Pfeifer, and W. Hölderich, Eds.), p. 1677, Studies in Surfactant Science and Catalysis, Vol. **84**, Elsevier, Amsterdam, 1994.
- Choudhary, V. R., *Chem. Ind. Dev.* **8**, 32 (1974).
- Choudhary, V. R., *Ind. Eng. Chem. Proc. Res. Dev.* **14**, 227 (1975).
- Szabo, J., Perrotey, J., Szabo, G., Duchet, J. C., and Cornet, D., *J. Mol. Catal.* **67**, 79 (1991).
- Leftin, H. P., Hermana, E., in "Proceedings, 3rd International Congress on Catalysis, Amsterdam, 1964, Vol. 2, p. 1064. Wiley, New York, 1965.
- Dent, A. L., and Kokes, R. J., *J. Phys. Chem.* **75**, 487 (1971).
- Chang, C. C., Conner, W. C., and Kokes, R. J., *J. Phys. Chem.* **77**, 1957 (1973).
- Radom, L., Pople, J. A., and Schleyer, P., *J. Am. Chem. Soc.* **95**, 8193 (1973).
- Kazansky, V. B., and Senchenya, I. N., *J. Catal.* **119**, 109 (1989).
- Kazansky, V. B., and Senchenya, I. N., *J. Mol. Catal.* **74**, 257 (1992).
- Haw, J. F., Richardson, B. R., Oshiro, I. S., Lazo, N. D., and Speed, J. A., *J. Am. Chem. Soc.* **111**, 2052 (1989).
- Gielgens, L. H., van Kampen, M. G. H., Broek, M. M., van Hardeveld, R., and Ponec, V., *J. Catal.* **154**, 201 (1995).
- Baker, B. G., and Clark, N. J., in "Catalysis and Automotive Pollution Control" (A. Crucq and A. Frennet, Eds.), Studies in Surfactant Science and Catalysis, Vol. **30**, p. 483. Elsevier, Amsterdam, 1994.
- Baker, B. G., Clark, N. J., Macarthur, H., and Summerville E., Int. Patent Appl., PCt AU87 00110, 1984.
- Parry, E. P., *J. Catal.* **2**, 371 (1963).
- Boehm, H. P., and Knözinger, H., in "Catalysis" (J. R. Anderson and M. Boudart, Eds.), Vol. **4**, p. 40. Springer, Berlin, 1983.
- Busca, G., Ramis, G., Lorenzelli, V., Janin, A., and Lavalley, J., *Spectrochim. Acta A* **43**, 489, (1987).
- Ledo, B., Rives, V., Sanchez-Escribano, V., and Busca, G., *Catal. Lett.* **18**, 329 (1993).
- Sanchez-Escribano, V., Busca, G., and Lorenzelli, V., *J. Phys. Chem.* **95**, 5541 (1991).
- Slinkin, A. A., Kharson, M. S., Dergachev, A. A., Udaltsova, E. A., and Ermolov, L. V., *Kinet. Catal.* **33**, 841 (1992).
- Yan, Y., Xin, Q., Jiang, S., and Guo, X., *J. Catal.* **131**, 234 (1991).
- Zaki, M., and Knözinger, H., *J. Catal.* **119**, 311 (1989).
- Henrich, V. E., and Cox, P. A., "The Surface Science of Metal Oxides." Cambridge Univ. Press, Cambridge, UK, 1993.
- Beaufils, J. P., and Barbaux, Y., *J. Chim. Phys.* **78** 347 (1981).
- Jacobs, J., Maltha, A., Reintjes, J. H. G., Drimal, J., Ponec, V., and Brongersma, H. H., *J. Catal.* **147** 294 (1994).