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On the Nature and Formation of the Active Sites in Re_2O_7 Metathesis Catalysts Supported on Borated Alumina

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Re_2O_7 catalysts on borated aluminas have been investigated with a view to correlating the structure of the active site and its activity in the methathesis of methyl oleate. Modification of alumina with boria results in much more active metathesis catalysts. Infrared spectroscopy was used for the characterization, pyridine adsorption measurements for determining the Lewis acid and Brønsted acid sites, and temperature-programmed IR measurements to follow the reactions occurring during calcination of the supports and catalysts. At a loading up to 5 wt% B_2O_3, an alumina phase is present together with a boria phase. Both phases contain surface hydroxyls. At higher B_2O_3 loadings (>5 wt%) the alumina hydroxyls are completely covered by boria. The amount of boron hydroxyls decreases with increasing B_2O_3 loading, due to the formation of linear boria polymers. Boria binds to the surface via the alumina hydroxyls. Upon Re_2O_7 loading of nonborated alumina, the ReO_4 groups react first with Lewis acid sites, onto which they are strongly bonded. Above a Re_2O_7 loading of 3 wt% surface hydroxyls are also substituted by ReO_4 groups, resulting in an increase in catalytic activity. When the borated supports are loaded with Re_2O_7, the ReO_4 groups are also first bonded to the Lewis acid sites. During calcination these ReO_4 groups substitute surface hydroxyls preferably on alumina hydroxyls. The substitution of the boron hydroxyls only takes place at a calcination time of at least 2 h at 823 K. At high borate loadings (>10 wt%) the reaction of ReO_4 groups with boron hydroxyls competes with the condensation reaction of two neighbouring boron hydroxyls. Taking into account that a ReO_4 group which has substituted an acidic OH group on the support is the precursor of an active site, the increase in activity of Re_2O_7 catalysts by modification of the alumina support with boria can be ascribed to two effects, namely, the reduction of the bonding strength of Lewis acid sites with ReO_4, making the ReO_4–OH substitution reaction possible during calcination even at low rhenium loadings, and the formation of acidic surface hydroxyls.

INTRODUCTION

Since the discovery in 1977 that $Re_2O_7/\gamma\text{-}Al_2O_3$ promoted with a small amount of tetramethyltin is active in the metathesis of functionally substituted alkenes, such as methyl oleate (1), much effort has been directed to the improvement of the activity of this catalyst system. First, the promoter has been investigated. It appeared that the use of other tetra-alkyltin and even tetra-alkyllead compounds resulted in an improved activity (2). The best promoters reported so far are tetraethyltin and tetrabutyltin. The use of other supports instead of γ-alumina also added to the improvement of the catalytic activity, especially for low-loaded (3 wt%) Re_2O_7-catalysts (3–6). For example, the use of silica–alumina as a support leads to a much higher catalytic activity (3). Improvements were also obtained when the γ-alumina support was modified either with another metal oxide, such as WO_3, MoO_3, and V_2O_5 (4), or with phosphate (5) or boria (6).

These modified alumina supports and silica-alumina have a more acidic character than alumina itself (5, 7). On this basis we developed the theory that the precursor of an active Re site is a ReO_4 group which has substituted an acidic OH group on the support (5, 8, 9). The resulting Re site will be relatively electron-poor and therefore it will easily allow the complexation of an electron-rich carbon–carbon double bond of the alkene, which is necessary for the propagation of the metathesis reaction. This theory was verified by means of infrared spectroscopy for Re_2O_7 supported on alumina and phosphated alumina (5). On Al_2O_3 Lewis acid sites (*c*oordinatively *u*n*s*aturated Al^{3+} sites (cus Al^{3+})) are present together with basic, neutral, and acidic hydroxyls (10). Upon impregnation with NH_4ReO_4, first coordination to Lewis acid sites takes place (Fig. 1a). These sites are inactive for metathesis. The structure of the site is not clear in detail. Probably it is essentially perrhenic acid adsorbed on cus Al^{3+}. Then the basic hydroxyls are preferably substituted with ReO_4 groups (Fig. 1b). At higher Re_2O_7 loadings acidic hydroxyls also are substituted (Fig. 1c). These sites exhibit a very high catalytic activity. A phosphated-alumina-supported catalyst shows high activity already at low Re_2O_7 loadings.

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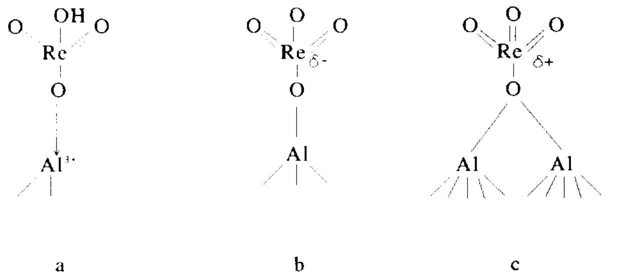

FIG. 1. Possible structures of ReO_4 groups on different sites of alumina. (a) Lewis acid site (hypothetical), (b) basic surface hydroxyl, and (c) Brønsted acidic surface hydroxyl. The catalytic activity of species a is negligible, of species b rather low and of species c very high.

This can be explained by the fact that already at low rhenium loadings acidic OH groups, either bonded to phosphorus or alumina, are substituted by ReO_4 groups (Fig. 1c).

Xu *et al.* (6) showed that modification of the alumina support with boric acid also leads to a large improvement of the catalytic activity for low-loaded Re_2O_7 catalysts in the metathesis of methyl oleate (6). It has been reported that the modification of alumina with boria results in the formation of a Brønsted acidic support (11, 12) and we assumed that ReO_4 groups replaced these acidic OH groups on the support, similar to the case of the phosphated alumina.

In this study we seek a correlation between the structure of the boria-modified alumina and the activity of low-loaded Re_2O_7 catalysts on these supports in the metathesis of methyl oleate. Metathesis of methyl oleate results in the formation of a normal alkene (9-octadecene) and a diester (dimethyl 9-octadecene-1,18-dioate);

$$\begin{aligned}2CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3 &\rightleftarrows \\ &CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3 \\ &+ CH_3OOC(CH_2)_7CH{=}CH(CH_2)_7COOCH_3. \quad [1]\end{aligned}$$

Infrared spectroscopy was used to characterize the supports and the catalysts based on them. The OH-stretch region was studied to determine the character of the OH groups present on the various supports, and to determine which OH groups were substituted by ReO_4 groups after impregnation. The relative amount and strength of Lewis acid sites was investigated by IR after pyridine adsorption. It will appear that borated alumina has a different behaviour from alumina. The ReO_4 groups on borated alumina are first bonded to the Lewis acid sites and subsequently react very slowly with the OH groups on the support. Temperature-programmed IR measurements were carried out to follow this reaction.

EXPERIMENTAL

Catalyst Preparation

The alumina support was γ-Al_2O_3 type CK-300 (BET surface area = 208 m^2/g; V_p = 0.51 cm^3/g) obtained from Akzo Chemicals bv. It was ground and sieved, and the 180–250 μm fraction was used. The boria-modified aluminas were obtained by multistep pore-volume impregnation of a sieved fraction (180–250 μm) of the γ-Al_2O_3 with an aqueous solution of H_3BO_3 (Brocades). Between two impregnation steps the support was dried at 383 K for at least 2 h. After the impregnation procedure the support was calcined by heating it to 688 K in an oxygen flow of 35 μmol/s (50 ml/min) at a rate of 10 K/min. Boria-modifed supports were prepared with calculated amounts of 5, 10, and 15 wt% B_2O_3, respectively. The supports are denoted AB5, AB10, and AB15, respectively.

The Re_2O_7 catalysts were prepared by pore-volume impregnation of the supports with an aqueous solution of ammonium perrhenate (Johnson Matthey Chemicals, Ltd., JMC 836 Specpure), followed by drying overnight in air at 383 K. Catalysts with a high Re_2O_7 loading were impregnated several times to obtain the desired loading. Between two impregnation steps the catalysts were dried at 383 K for 2 h. The 3 wt% Re_2O_7 catalysts are denoted Re3, the 6 wt% Re_2O_7 catalysts as Re6. Thus, 3 wt% Re_2O_7 on borated alumina with 10 wt% B_2O_3 is denoted Re3/AB10.

Properties of the calcined supports and catalysts are given in Table 1.

Activity Measurements

The metathesis reactions were carried out as described earlier (8). 100 mg of catalyst was first calcined by heating it to 823 K in an oxygen stream of 35 μmol/s (50 ml/min) at a rate of 20 K/min. After 2 h at this temperature the catalyst was cooled to room temperature (297 K). It was then transferred into the glass reaction vessel with a capacity of 30 ml and placed under an argon atmosphere. Subsequently, a solution of hexane, containing tetrabutyltin, and methyl oleate were added in that order. All experiments were carried out at room temperature (297 K). The molar ratio of methyl oleate to Re to $Sn(C_4H_9)_4$ to hexane was 240/1/0.6/625 in all cases.

In a typical experiment 100 mg of catalyst was used to which 1 ml of hexane, containing 2.46 μl (7 μmol) of tetrabutyltin, and 1 ml (2.9 mmol) of methyl oleate for a 3 wt% Re_2O_7 catalyst were added. For a 6 wt% Re_2O_7 catalyst double the amounts were added.

The reaction was monitored by GC analysis (Carlo Erba HRGC 5300 Mega Series) of the liquid phase over a capillary column (J&W Scientific, DB1, 30 m × 0.53 mm i.d., film thickness 1.5 μm). The GC signals were processed by

TABLE 1

Properties of the $Al_2O_3 \cdot B_2O_3$ Supports after Calcination at 688 K and Catalysts Based on These Supports after Calcination at 823 K

B_2O_3 content of the support		Re_2O_7 loading			Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore radius (nm)
Nom.[a] (wt%)	As number of B atoms/nm^2	Nom.[a] (wt%)	Meas.[b] (wt%)	As number of Re atoms/nm^2[c]			
0	0	0	—	0	206	0.50	4.2
		3	3.0	0.36	205	0.48	4.2
		6	6.1	0.73	205	0.48	4.0
5	4.2	0	—	0	204	0.49	3.5
		3	3.0	0.35	212	0.45	3.7
		6	6.2	0.74	208	0.42	3.3
10	8.3	0	—	0	208	0.47	3.5
		3	3.0	0.35	215	0.40	3.3
		6	5.6	0.66	209	0.41	3.3
15	13.8	0	—	0	188	0.40	3.3
		3	0.80	0.13	154	0.36	3.6
		6	2.3	0.46	125	0.30	3.3

[a] Nominal (i.e., calculated) amount.

[b] Measured by ICP-AES, as described earlier (8).

[c] Calculated from the measured Re_2O_7 loading and BET surface area.

a Shimadzu C-R5A Chromatopaq integrator. The methyl oleate conversions were calculated as (2 × alkene)/(2 × alkene + methyl oleate) from the peak areas of the GC analyses, which were corrected for the molecular response by Ackman's method (13, 14).

Infrared Measurements

Before the IR spectra were recorded, the catalysts were calcined in oxygen (60 ml/min) at 823 K for 2 h (heating rate 20 K/min) and subsequently exposed to air. IR spectra were recorded on a Digilab FTS 15E spectrometer, using self-supporting disks of a 20-mg sample (approximately 8 mg cm^{-2}). The standard procedure for recording an IR spectrum consisted of a heat treatment at 773 K in vacuum during 0.75 h. This is the same procedure as has been applied in our study of phosphated aluminas (5).

The temperature-programmed IR measurements were performed with wet samples, which were dried at 398 K during 0.75 h under vacuum before a spectrum was recorded. Subsequently, they were heated to the next drying/calcination temperature and kept at that temperature for 0.75 h; after the samples were cooled to room temperature, the IR spectrum was recorded.

Pyridine adsorption was used to determine the presence of Lewis and Brønsted acid sites on the supports. For the determination of the strength of the Lewis acid sites, an IR spectrum was recorded after pyridine adsorption at 423 K and subsequent cooling to room temperature. Thereafter part of the pyridine was desorbed by heating the sample to 523 K. After it was cooled to room temperature, a new IR spectrum of the sample was recorded.

RESULTS AND DISCUSSION

Activity Measurements

In Fig. 2 the effect of the support on the activity of Re3 catalysts (Fig. 2a) and Re6 catalysts (Fig. 2b) in the metathesis of methyl oleate is shown. It is clear that the modification of the alumina support with boria results in catalysts with a higher activity. For the Re3 catalysts it appears that AB10 gives the most active catalyst, while for the Re6 catalysts AB5 gives a slightly better catalyst than AB10. The low activities of the catalysts on AB15 can be mainly ascribed to excessive Re losses (>50%), probably during calcination (see Table 1).

The Re3 and Re6 catalysts can be compared directly, as the molar ratios of methyl oleate to Re were kept constant. In all cases, except for AB10, the Re6 catalyst shows a higher activity than the Re3 catalyst on the same support.

In Fig. 3 we compare the activity of Re3 catalysts on three different supports, viz. alumina, phosphated alumina (2.2 wt% P) and AB5. The catalysts on the modified aluminas show a higher activity than the alumina-supported catalyst. The activity of the catalyst on AB5 had

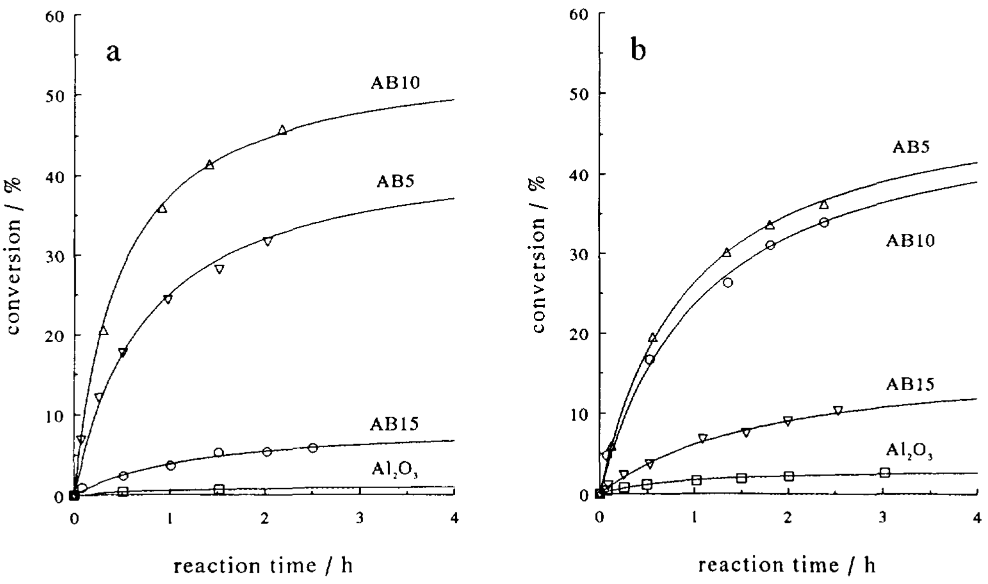

FIG. 2. Conversion of methyl oleate as a function of reaction time at 297 K. Molar ratio methyl oleate/Re/Sn(n-C_4H_9)$_4$/hexane = 240/1/0.6/625. The codes in the figures denote the support: (a) Re3 catalysts and (b) Re6 catalysts.

an even higher activity than the phosphated alumina. This difference is explained later.

Raman Spectroscopy

An attempt has been made to record Raman spectra of the borated supports and the Re_2O_7 catalyst on these supports. This proved impossible, due to high fluorescence of the samples. Individually Al_2O_3 and orthoboric acid do not show any fluorescence, but the combination does. This may be due to traces of chromium in the alumina, which are forced towards the surface after impregnation with boric acid and subsequent calcination. It is well known that chromium compounds exhibit a high fluorescence.

Infrared Spectroscopy

The IR spectrum of γ-Al_2O_3 consists of three main bands which can be ascribed to basic OH groups (3775 cm^{-1}), neutral OH-groups (3730 cm^{-1}) and acidic OH-groups (3690 cm^{-1}), respectively (10). The standard IR spectra of the supports are shown in Fig. 4, and those of the Re3 catalysts on these supports are shown in Fig. 5.

When we consider the spectra of alumina and its Re3 counterpart, we do not see a decrease in the absorbances of the OH groups, but an increase. We therefore conclude that the ReO_4 groups have reacted with the Lewis acid sites on the support (Fig. 1a) rather than with OH-groups.

Figure 4 shows that a new surface hydroxyl is formed when Al_2O_3 is modified with B_2O_3. The new surface hydroxyl is a hydroxyl bonded to boron, for which the IR absorption is at 3695 cm^{-1}. The absorbances of both Al–OH and B–OH groups decrease with increasing B_2O_3 loading (after evacuation at 773 K; see Table 2).

It was checked separately whether B_2O_3 is bonded to Lewis acid sites. Although themselves invisible in IR, Lewis acid sites can be determined easily by pyridine adsorption (7). Table 3 gives the intensities of a band characteristic for adsorption of pyridine to Lewis acid sites. From these data we conclude that B_2O_3 is not bonded onto Lewis acid sites, because their amount does not decrease smoothly with increasing boria loading. We therefore conclude that boria is bonded onto the Al–OH groups. This is supported by the standard IR spectra of the supports (Fig. 4). On AB5 a significant amount of Al–hydroxyls is still present together with the newly formed boron hydroxyls, but at higher B_2O_3 loadings only boron hydroxyls could be detected. Our interpretation is that B_2O_3 forms a monolayer of linear B_2O_3 chains with OH-groups on the edges (Fig. 6).

Upon loading of the borated supports with rhenium no decrease in the absorption band of the B–OH groups is observed in the standard IR spectra (Fig. 5 and Table 2). For the catalyst based on AB5 only the absorbances of all aluminum-bonded hydroxyls are strongly decreased, which indicates that the ReO_4 groups have reacted with the Al–OH groups. This is surprising, because one would expect that the ReO_4 groups first bind to the Lewis acid sites, as in the case of the alumina-supported catalyst. As the Lewis acid sites are not blocked by B_2O_3, we conclude that the presence of B_2O_3 has weakened the bonding of ReO_4 groups with Lewis acid sites. The replacement of

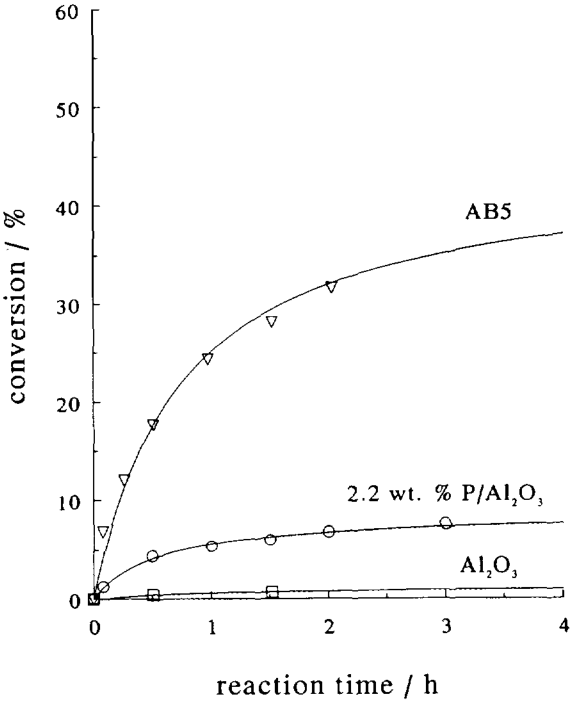

FIG. 3. Conversion of methyl oleate as a function of reaction time at 297 K for Re3 catalysts on alumina, phosphated alumina, and borated alumina. The text in the figure denotes the support. Molar ratio methyl oleate/Re/Sn(n-C_4H_9)$_4$/hexane = 240/1/0.6/625.

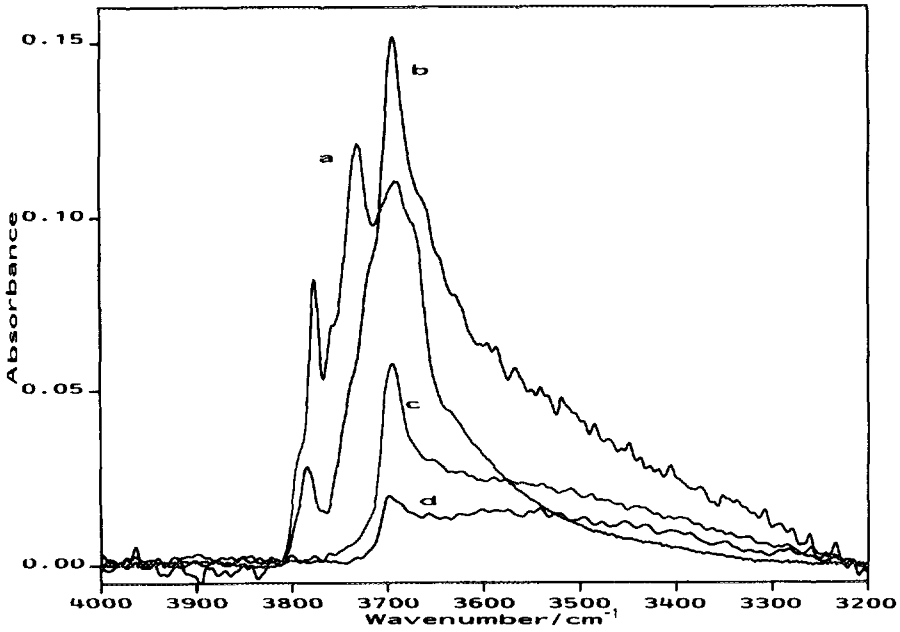

FIG. 4. Standard IR spectra of the supports: (a) Al_2O_3, (b) AB5, (c) AB10, and (d) AB15.

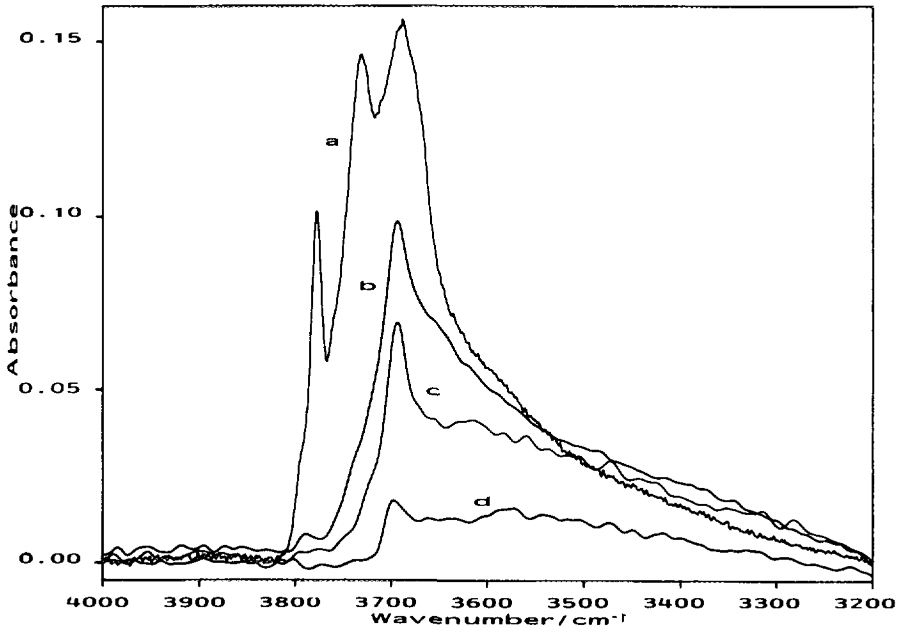

FIG. 5. Standard IR spectra of Re3 catalysts on the supports of Fig. 4: (a) Al_2O_3, (b) AB5, (c) AB10, and (d) AB15.

aluminium-bonded hydroxyls (basic, neutral, and acidic) instead of Lewis acid sites upon loading with Re_2O_7, results in a more active catalyst than the corresponding alumina-supported catalyst.

For the catalyst based on AB10 and AB15 a different conclusion has to be drawn. On these supports no Al-bonded OH groups are present. Moreover, the amount of B–OH does not decrease upon Re_2O_7 loading. Therefore we conclude that in these cases the ReO_4 groups are bonded to Lewis acid sites on the support. As these catalysts are rather active, the question arises as to how the active sites on these supports are formed. It is not likely that ReO_4 bonded to Lewis acid sites would form active metathesis sites, because ReO_4 bonded to Lewis acid sites on Al_2O_3 does not show any activity (5).

From the foregoing measurements no definitive conclusions could be drawn about the formation of active sites for borated aluminas with higher B_2O_3 loadings (≥ 10 wt%). Therefore, the catalyst preparation process was examined more closely. After impregnation of Al_2O_3 with a solution of orthoboric acid, the supports are calcined at 688 K. Then they are impregnated with an aqueous solution of ammonium perrhenate. So the supports are rehydrated when ammonium perrhenate is added. When we record the standard spectra, the catalysts are pretreated at high temperature *in vacuo*. It might well be that our results are not representative. Therefore, we also carried out pyridine adsorption measurements on rehydrated samples at 423 K. Indeed, Brønsted acidic sites

TABLE 2

Integrated Intensities of the B–OH Band (3695 cm^{-1}) for various Supports and Catalysts in Figs. 4 and 5

B_2O_3 loading (wt%)	IR absorbance of B–OH group	
	Support	Re3 catalyst
5	0.11^a	0.10^a
10	0.06	0.07
15	0.02	0.02

[a] Corrected for the absorbances of the Al–OH groups. The B–OH group and the Al–OH group have been separated by Gaussian analysis based on the absorbance of the Al–OH groups at 3730 cm^{-1}.

TABLE 3

Integrated Intensities of the 1620-cm^{-1} Band upon Adsorption of Pyridine[a]

Sample	Temperature (K)	
	423	523
γ-Al_2O_3-CK-300	2.1	1.1
AB5	3.2	1.7
AB10	2.3	0.9

[a] The 1620-cm^{-1} band is attributed to pyridine adsorbed on Lewis acid sites.

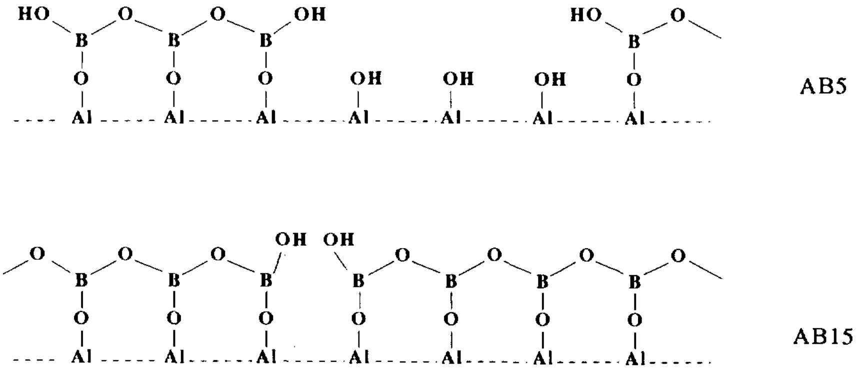

FIG. 6. Boria structures at different loadings on alumina.

were found on "wet" AB10 (absorbance at 1540 cm^{-1}). Upon calcination these sites disappear through condensation of two hydroxyls to water and a B–O–B bond. This suggests that not all available OH groups, that can be substituted by ReO_4 groups, are detected in the standard IR measurements. The similarity between the standard IR spectra of Re3/AB10 and Re3/AB15 and their respective supports can thus be explained by the reaction of ReO_4 groups with OH groups, which otherwise disappear by condensation during calcination.

Temperature-Programmed IR Spectroscopy

In order to determine what happens during calcination, we performed a temperature programmed IR study of the supports and the catalysts. The spectra were recorded after heating the sample *in situ* at various temperatures. In Fig. 7 the IR spectra of the "wet" samples at 431 K are shown. Comparing the spectra of pure Al_2O_3, 3 wt% Re_2O_7/Al_2O_3 and 6 wt% Re_2O_7/Al_2O_3 it can be concluded that the spectra of Al_2O_3 and 3 wt% Re_2O_7/Al_2O_3 are very similar. The amount of H_2O adsorbed (absorbance at 3585 cm^{-1}) is comparable. However, for 6 wt% Re_2O_7/Al_2O_3 the adsorption of H_2O is much higher. On the Re3 catalyst structure 1a is predominantly present, whereas on Re6/Al also Al-bonded OH groups are substituted by ReO_4 groups. Apparently, ReO_4 groups which are not bonded to Lewis acid sites increase the hygroscopic character of the catalyst.

The "wet" samples give the spectra of the Re═O vibrations around 1000 cm^{-1} (Fig. 8). Almost no IR absorbance is observed for Re3/Al (structure 1a), whereas for Re6/Al (structure 1b) there is a clear absorption band. When we compare the "wet" borated catalysts (at 431 K) with the alumina-supported catalysts, we can conclude that their Re═O IR spectra are similar to that of 3 wt% Re_2O_7/Al_2O_3. This indicates that the ReO_4 groups are mainly bonded to Lewis acid sites after standard preparation, which consists of impregnation and subsequent drying at 383 K.

The IR spectra of the OH-stretch region of the "wet" borated supports and catalysts on these supports are also given in Fig. 7. No significant difference is observed between the IR spectra of the support and the Re3 catalyst on that support for all borated aluminas, again indicating that the ReO_4 groups are bonded to Lewis acid sites. This is also the case for Re3/AB5. During calcination of this catalyst the ReO_4 groups react with the aluminium-bonded surface hydroxyls, indicating that the bonding between the Lewis acid sites and the ReO_4 groups on this catalyst is not as strong as on alumina-supported catalysts. Since upon rehydration the original IR spectrum is obtained, it is clear that for this catalyst the substitution of the surface hydroxyls with ReO_4 groups is reversible.

In Fig. 9 the temperature-programmed IR spectra of 10 wt% B_2O_3/Al_2O_3 and the 3 wt% Re_2O_7 catalyst on this support are compared. At low temperatures (≤ 523 K) no difference in the IR spectra can be observed. However, at 773 K the B–OH absorption band has nearly disappeared, while it is clearly present on the support. We conclude that the ReO_4 groups have substituted the boron hydroxyls of the support, but that this reaction proceeds very slowly. When we recorded the standard spectra (after heating at 773K during 0.75 h) we did not observe a decrease in the absorption band of the B–OH groups (see Fig. 4). To check these different results, we carried out IR measurements of a sample which was first treated according to the standard procedure (773 K, 0.75 h) and subsequently heated for 2 h at 773 K. This experiment confirmed our previous observations. After the standard procedure no decrease in the absorption band of the B–OH groups was observed, but after the more severe conditions the B–OH absorption band had disappeared almost completely. The same experiment was also performed with Re3/AB5. For this catalyst, essentially no difference between the two spectra was observed (see Fig. 10). This result is not surprising, because on AB5 the ReO_4 groups mainly react with the Al–OH groups that are available on the support in sufficient amounts.

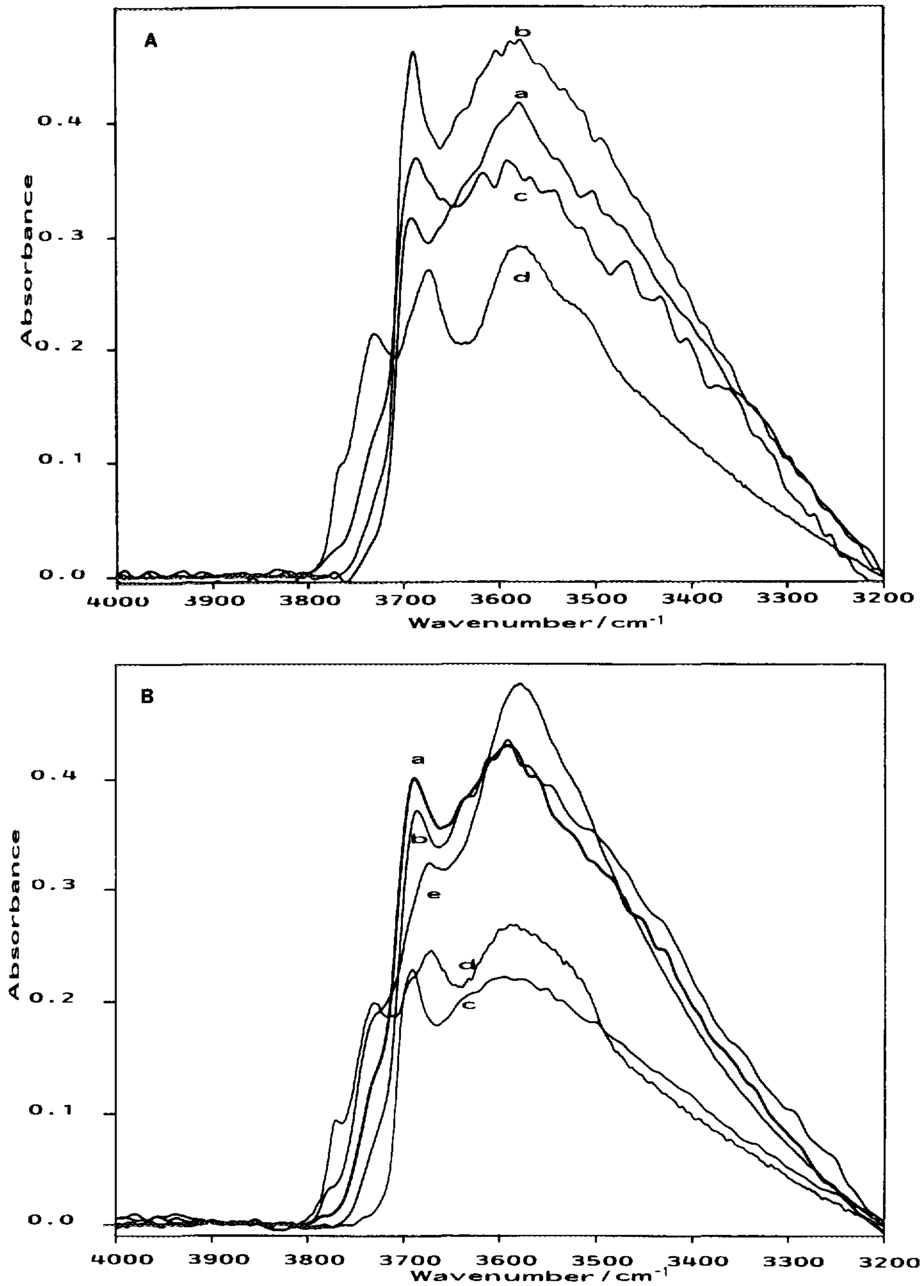

FIG. 7. IR spectra of samples, dehydrated at 431 K. (A) Supports: (a) AB5, (b) AB10, (c) AB15, and (d) Al_2O_3. (B) Re3 catalysts on: (a) AB5, (b) AB10, (c) AB15, and (d) Al_2O_3. For comparison, Re6/Al is also given (e).

After rehydration of Re3/AB10 at 423 K (i.e., leaving it overnight in the *in situ* IR cell under ambient conditions) a different IR spectrum was obtained compared to the original "wet" spectrum shown in Fig. 7. After a day the original "wet" IR spectrum is obtained, indicating that the substitution of boron hydroxyls by ReO_4 is also a reversible reaction, although a very slow one.

On AB15 the amount of surface hydroxyls is already low (Fig. 7). Upon calcination of this support the low amount of B–OH groups present condense with each other, leaving no surface hydroxyls at the support. From Table 1 it is clear that rhenium is not very well retained on this catalyst. During calcination of the catalyst two processes occur at the same time:

$$2\text{B–OH} \leftrightarrows \text{B–O–B} + H_2O \qquad [2]$$

$$\text{B–OH} + HReO_4 \leftrightarrows \text{B–OReO}_3 + H_2O. \qquad [3]$$

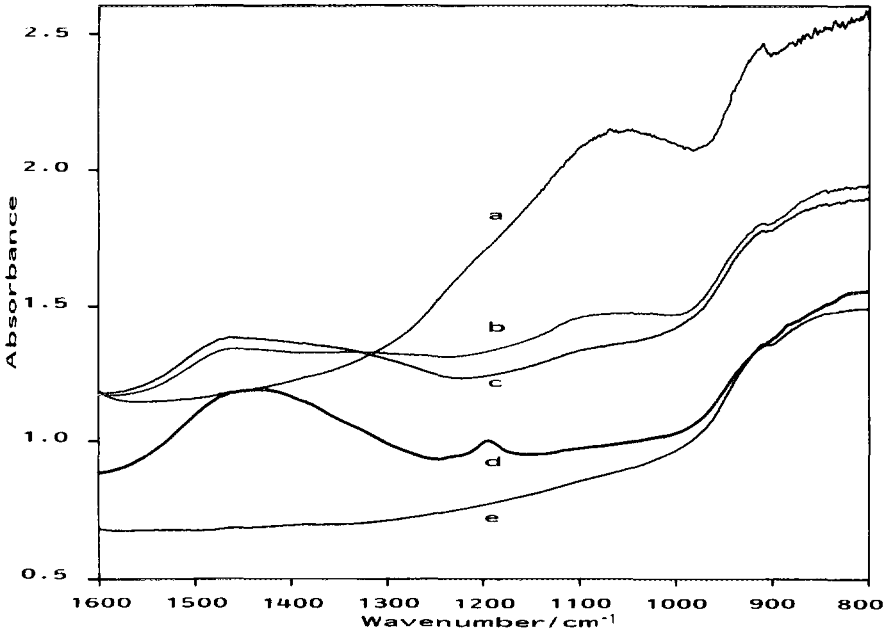

FIG. 8. IR spectra of supported Re_2O_7 catalysts, dehydrated at 431 K: (a) Re6/Al, (b) Re3/AB5, (c) Re3/AB10, (d) Re3/AB15, and (e) Re3/Al.

From the results with AB10 we concluded that the reaction [3] of ReO_4 with B–OH is rather slow. The condensation reaction [2] competes with reaction [3], resulting in considerable rhenium losses as unreacted rhenium is rather volatile. Upon rehydration of the catalyst, the original "wet" spectrum is slowly formed back, as we also observed for AB10.

There formation of the original "wet" catalyst upon rehydration of the calcined catalyst is confirmed by experiments with Re6/AB15. After calcination of this catalyst the Re_2O_7 loading was 2.3 wt%. This catalyst was stored and exposed to air for at least two weeks. Then the catalyst was calcined again for 2 h at 823 K and an IR spectrum was recorded. No B–OH absorption bands or Re═O vibrations were found. The Re_2O_7 loading after this second calcination step was determined by XPS and was approximately 0.5 wt%. Thus, the Re2.3/AB15, obtained after a single calcination step of Re6/AB15, behaves in the same way as the fresh Re3/AB15 sample.

In Fig. 11 the Re═O vibrations are shown for the various catalysts after the heat treatment at 773 K during 2 h. There is no difference for Re3/Al and Re6/Al in the position of the absorption bands (998 and 1018 cm^{-1}) or in the ratio of the two bands. Therefore from IR no discrimination can be made between ReO_4 groups bonded to Lewis acid sites and ReO_4 groups that have substituted surface hydroxyls. The borated samples do however show a different ratio of the two absorption bands, which could be related with the different bonding of the ReO_4 groups.

Effect of the Re_2O_7 Loading

All IR measurements have been performed on Re3 catalysts, except for the alumina-supported catalyst. We have seen that on Al_2O_3-supported catalysts the ReO_4 groups first react with Lewis acid sites, which does not result in metathesis active sites. At a Re_2O_7 loading of 6 wt%, basic OH-groups are replaced by ReO_4, and at higher loadings the neutral and acidic OH-groups are also substituted by ReO_4. The metathesis activity increases sharply with increasing Re_2O_7 loading. From these facts we drew the conclusion that the substitution of an acidic OH-group is a prerequisite for a metathesis active site (5).

From the activity measurements we can see that the Re6 catalysts on all supports, except for AB10, are more active than the Re3 catalyst on the same support. For Al_2O_3-supported catalyst this was already explained. The IR spectrum of AB5 shows that at a Re_2O_7 loading of approximately 3 wt% the remaining aluminium hydroxyls are substituted with ReO_4. At higher Re_2O_7 loadings the "excess" of ReO_4 groups probably substitutes B–OH groups. As the percentage of substituted acidic OH groups (acidic alumina and boron-bonded hydroxyls) is increased, the activity also increases. For AB15 the difference in activity can be explained by the loss of rhenium upon calcination.

Re3/AB10 is more active than the Re6 catalyst on the same support. A significant Re loss for the Re6 catalyst was observed, in contrast to the Re3 catalyst, where no Re was lost. As the calculated molar ratios of methyl oleate to rhe-

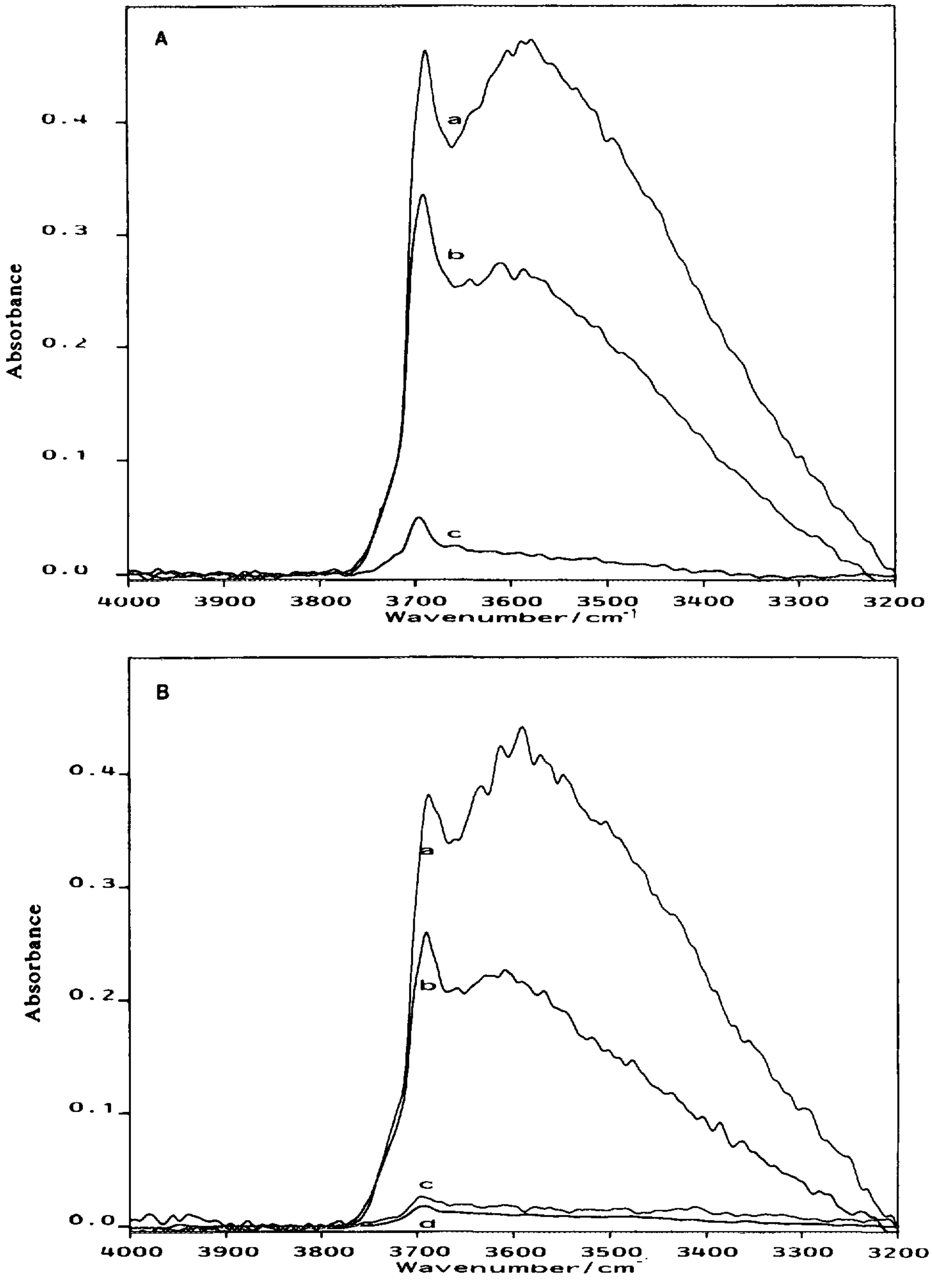

FIG. 9. IR spectra of AB10 (A) and Re3/AB10 (B) at various recording temperatures: (a) 431 K, (b) 523 K, (c) 773 K (standard), and (d) 773 K for 2 h.

nium were kept constant, the loss of rhenium results in a higher molar ratio of methyl oleate to rhenium for the Re6 catalyst, compared to the Re3 catalyst, and, therefore, an apparent lower activity for the Re6 catalyst is found.

The Re loss on the Re6 catalyst can be explained as follows. On the Re3 catalyst the ReO_4 groups bind to all "free" B–OH groups on the support (i.e., the remaining B–OH groups on the support after calcination of 2 h at 823 K; see Fig. 4). At higher Re_2O_7 loadings the "excess" of ReO_4 groups has to compete with the condensation reaction [2] of the boron hydroxyls, similar to those on AB15. The significant rhenium loss observed for Re6/AB10 supports the idea that two competing reactions occur.

Comparison of Phosphated and Borated Aluminas as Supports

From Fig. 3 it is clear that the use of a borated alumina instead of a phosphated alumina leads to a more active

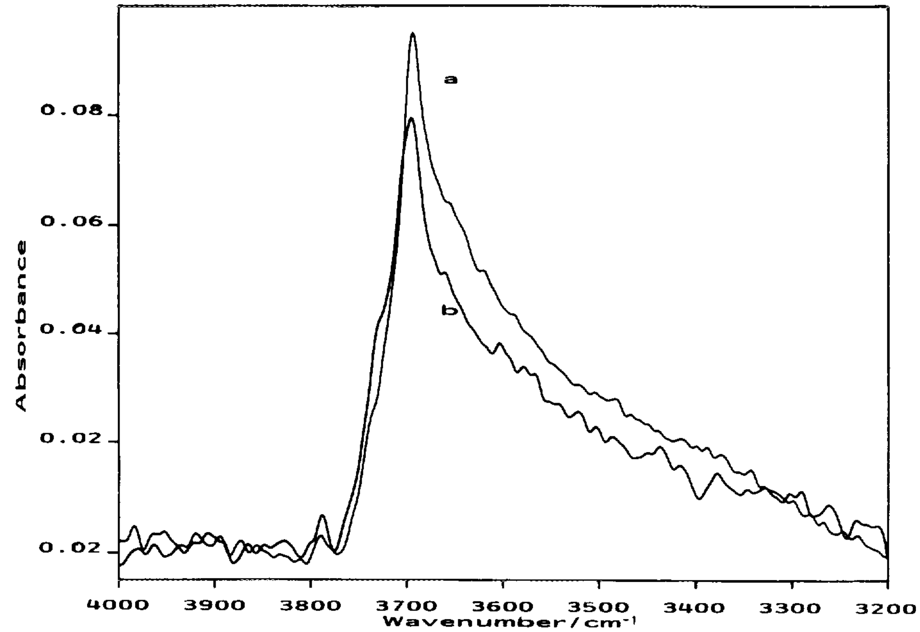

FIG. 10. IR spectra of Re3/AB5: (a) standard spectrum at 773 K and (b) spectrum after 2 h at 773 K.

catalyst at low Re_2O_7 loadings. In a previous study (5) the phosphated support and catalysts based upon this support were characterized by IR spectroscopy. From this study it appeared that already at a Re_2O_7 loading of 3 wt% all types of hydroxyls on the support (basic, neutral and acidic) are equally replaced with ReO_4. The immediate decrease in the amount of hydroxyls on the phosphated support indicates that the Lewis acid sites on alumina do not have such a strong bonding with ReO_4 groups after the phosphate treatment. We assumed that on Al_2O_3 up to a Re_2O_7 loading of 3 wt% the ReO_4 groups are strongly bonded onto Lewis acid sites. This Re_2O_7 loading corresponds to 0.12 mmol of Re atoms per g of catalyst or 0.36 Re atoms per nm^2. The phosphated alumina contained 2.2 wt% P, which corresponds to 2.7 P atoms per nm^2 of catalyst. The phosphate reacts probably with acidic OH groups on alumina (5), but it does not bind to Lewis acid sites on alumina (15), so these sites are still present on the phosphated support.

The amount of hydroxyls on the surface of Al_2O_3-CK-300 is about 10.7 hydroxyls per nm^2 of support at 473 K (10). The amount of phosphate on the support is far less than this value. Thus, a large part of the support still contains surface hydroxyls of alumina. A part of the acidic hydroxyls have been replaced by phosphate, which results in the creation of a new type of OH group, bonded to phosphorus.

As discussed before, the catalytic activity of the catalysts on the borated supports is better than that of the phospated support. It should be noted that the amount of boria is much higher than the amount of phosphate. AB5 contains 4.2 boron atoms per nm^2 of catalyst, 1.5 times as many as the phosphated catalyst. The modification of the support with boria results in a weaker bonding of the Lewis acid sites with ReO_4 groups. The difference in activity between the phosphated and borated catalyst can, at least partly, be ascribed to the difference in the amount of modifier. On the borated Al_2O_3, a larger part of the ReO_4 groups has substituted an acidic hydroxyl compared to the phosphated catalyst, which still contains a considerable amount of basic hydroxyls.

We suppose that boria forms linear polymeric structures on the support (see Fig. 6). The length of the polymers will increase with increasing B_2O_3 loadings. XRD measurements of the supports we used could not detect the presence of B_2O_3 crystallites or Al borate. We suggest that the boron hydroxyls are located at the border of the boria polymers. In the case of the phosphated catalyst we suppose that isolated phosphate groups are present and that no polymeric structures have been formed, because the phosphate loading is rather low.

The conclusion which can be drawn from the modification of alumina with relatively low loadings of boria or phosphate is that the bonding strength of the Lewis acid sites with ReO_4 groups is reduced. Apparently, the substitution of surface hydroxyls by ReO_4 is more favourable than the bonding of ReO_4 to Lewis acid sites, but in the case of alumina the activation energy is too high to allow this reaction at 823 K. An indication that this is indeed the case was found by Spronk (16). The calcination of Al_2O_3-supported Re_2O_7 catalysts at very high tempera-

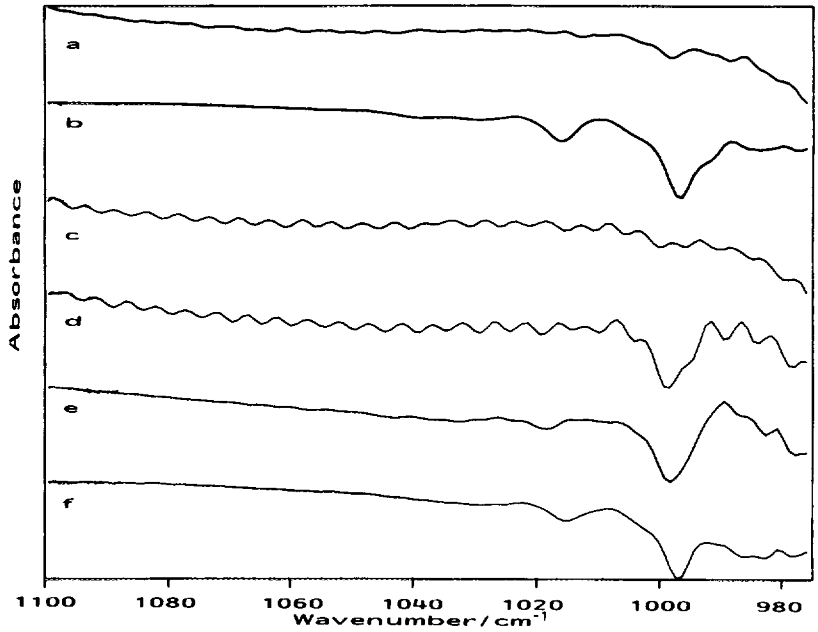

FIG. 11. IR spectra of supported Re_2O_7 catalysts after 2 h at 773 K: (a) Re6/AB15, (b) Re6/Al, (c) Re3/AB15, (d) Re3/AB10, (e) Re3/AB5, and (f) Re3/Al.

tures (around 1173 K) resulted in more active catalysts. This indicates that at these temperatures ReO_4 groups originally bonded to Lewis acid sites have substituted surface hydroxyls. The highest increase in activity was obtained for low-loaded catalysts, which would be expected because the low-loaded catalysts have a relatively high amount of ReO_4 groups bonded to Lewis acid sites.

The increase in catalytic activity with borated or phosphated supports can thus be ascribed to two effects, namely, the reduction of the bonding strength of the Lewis acid sites with ReO_4 and the formation of extra acidic surface hydroxyls.

CONCLUSIONS

The combination of pyridine adsorption and IR spectroscopy provides information about both the surface hydroxyls and Lewis acid sites. The temperature-programmed IR measurements give additional information about possible reactions during calcination of the catalyst. From this study it is very clear that different pretreatments of the catalyst for reaction and IR measurements (calcination) can result in misleading data.

The modification of γ-alumina with boria leads to an improved activity of low-loaded Re_2O_7 catalysts. The optimal B_2O_3 content is approximately 10 wt% (8.3 boron atoms per nm^2). Modification of the alumina with boria leads to the formation of boron hydroxyls, while the original alumina hydroxyls become covered with boria. At low B_2O_3 contents (<5 wt%) an alumina phase is present together with a boria phase. At higher B_2O_3 loadings the alumina hydroxyls are completely covered by boria. The amount of boron hydroxyls decreases with increasing B_2O_3 loading. The boria phase consists of linear B_2O_3 polymers, bonded to alumina, with the surface hydroxyls at the borders of these polymeric structures.

Upon Re_2O_7 loading of an alumina support the ReO_4 groups first react with Lewis acid sites, onto which they are strongly bonded. Above a Re_2O_7 loading of 3 wt% also surface hydroxyls are substituted by ReO_4 groups, resulting in an increase in catalytic activity.

When the borated supports are loaded with Re_2O_7, the ReO_4 groups are also initially bonded to the Lewis acid sites (prior to calcination). During calcination the ReO_4 groups substitute surface hydroxyls. On supports with a low B_2O_3 content (<5 wt%) there are still considerable amounts of alumina hydroxyls present, which react much faster with ReO_4 than boron hydroxyls. The substitution of boron hydroxyls by ReO_4 groups only takes place during calcination for at least 2 h at 823 K. The rehydration of ReO_4 groups that have replaced boron hydroxyls is also a very slow process, while the rehydration of ReO_4 groups that have replaced alumina hydroxyls proceeds very rapidly. Both reactions are completely reversible.

On the borated supports with a high B_2O_3 content (>10 wt%) the substitution of boron hydroxyls by ReO_4 groups competes with the condensation reaction of boron hydroxyls. The reverse of the latter reaction upon rehydration also occurs, though at a rather slow rate.

The increase in activity of Re_2O_7 catalysts by modification of the support with boria can be attributed to reduction of the bonding strength of the Lewis acid sites with ReO_4 and formation of acidic surface hydroxyls.

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