

An Infrared Spectroscopic Study of the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ Metathesis Catalyst

II. Catalytic Properties

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Propene, butene and higher alkenes reduce a $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ metathesis catalyst at ambient temperatures and subatmospheric pressures, while ethene shows hardly any reduction capacity under these conditions. The metathesis activity is generated by this reduction. By reduction a small activity for the polymerization of ethene to high-molecular weight linear polyethene is generated as well. Reduction of the catalysts with CO or NH_3 at temperatures between 300 and 500°C does not result in activity for the metathesis reaction. At room temperature NO adsorbs on the reduced catalyst (ir bands at 1768, 1790, 1860, and 1880 cm^{-1}) while CO does not. NO proved to be a poison for the metathesis reaction and by measuring the amount of adsorbed NO it was found that in the case of a catalyst with a complete monolayer of Re_2O_7 , less than 0.3% of the Re atoms were active. By the reduction of the catalyst with alkenes water is generated which is for the greater part associatively adsorbed. This water exchanges hydrogen atoms with propene and butene at ambient temperatures. When pyridine is adsorbed on a surface on which associatively adsorbed water is present, pyridinium ions are formed.

INTRODUCTION

In Part I (1) the structure and some physicochemical properties of the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ metathesis catalyst have been discussed. In this part we report the results of an *in situ* infrared spectroscopic study of the catalytic properties of this catalyst and the interaction of alkenes with the catalyst surface. To date no other infrared study of this catalyst has been reported.

METHODS

C_2D_4 was prepared by reacting $\text{C}_2\text{D}_4\text{Br}_2$ (Fluka) with Zn according to the procedure of Leitch and Morse (2). Mass spectrometry showed a purity of 98%, the remaining being $\text{C}_2\text{D}_3\text{H}$. Deuterated butene was prepared by dimerization of C_2D_4 with a $\text{NiO}_2/\text{Al}_2\text{O}_3/\text{SiO}_2$ catalyst at ca. 323 K.

After distillation a product mixture was obtained containing butene-1 (4%), trans-butene-2 (66%), *cis*-butene-2 (26%) and C_2D_4 (4%). By mass spectroscopy it was found that 98% of the butene was C_4D_8 and the rest $\text{C}_4\text{D}_7\text{H}$. NO (J. T. Baker, purity 99.5%) was dried on P_2O_5 and subjected to several freeze-thaw cycles until the frozen NO was snow white. CO (J. T. Baker, 99.0%) was dried on P_2O_5 . Pyridine (Fluka, 99.8%) was dried on P_2O_5 and outgassed by freeze-thaw cycles and ethene, propene and butenes (J. T. Baker) were purified in the same way.

Calcination of the catalyst was carried out by oxidizing with oxygen (723 K, 13.3×10^3 Pa, 1 hr), followed by 1 hr pumping at the same temperature. Sampling required for gas chromatographic

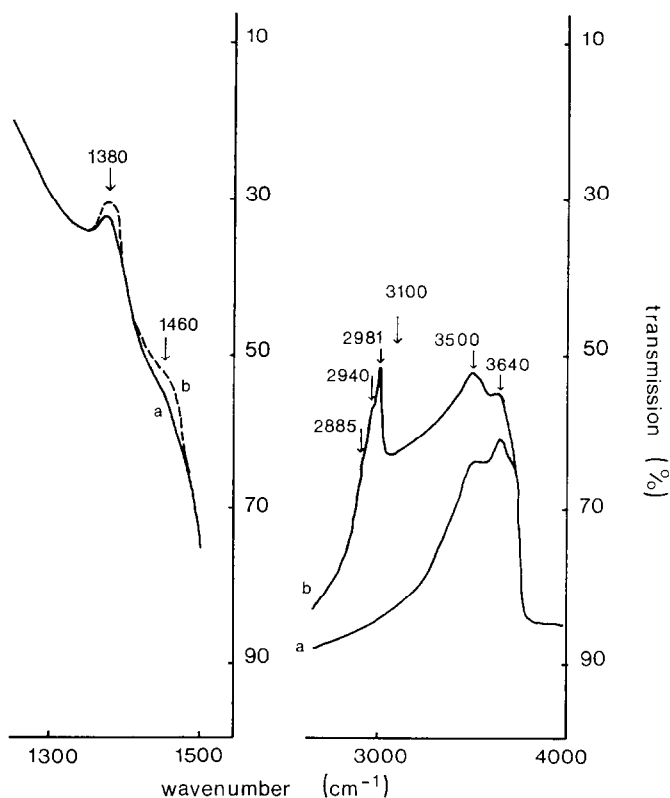


FIG. 1. Irreversible adsorption of propene on a $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst at ambient temperature. (a) Spectrum of the fresh catalyst; (b) 14 hr after exposing the catalyst to propene (13×10^3 Pa). Gaseous reactants have been pumped for 1 hr at ambient temperature.

analysis was effected by freezing the gaseous reactants in a separate vessel equipped with a septum. After thawing, samples were obtained with a hypodermic syringe.

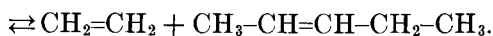
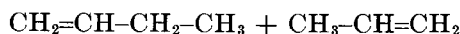
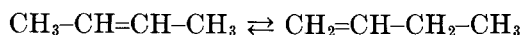
Other experimental details are described elsewhere (1).

RESULTS

1. Adsorption of Alkenes on the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ Catalyst

A few minutes after introducing at ambient temperatures an amount of propene into the infrared cell containing a calcined catalyst, the infrared spectrum of the gaseous reactants showed the characteristic 949 cm^{-1} band of ethene. That metathesis had occurred was confirmed by glc analysis of the gaseous reactants: ethene and butene-2 were found. After a few

hours butene-1, pentenes and hexenes were found, too. These species presumably originate through a combination of cross metathesis and double-bond shift reactions:



This scheme is supported by the observation that double-bond migration is catalyzed by $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$: a few minutes after contacting a fresh catalyst at ambient temperatures with butene-2, butene-1 was found. Owing to this dual activity it was not possible to study propene and butene adsorption separately in our apparatus. When writing about the adsorption of, for instance, propene, this will indicate that propene was the initial reactant.

Figure 1 shows the infrared spectrum of the catalyst 14 hr after introduction of propene (13.3×10^3 Pa) at ambient temperatures into the cell. Before recording the spectrum, the gaseous reactants (25% ethene, 40% propene, 26% butene, 8% pentene, and 1% hexene) had been pumped off for 1 hr at ambient temperatures. The species remaining on the catalyst surface are considered as irreversibly adsorbed. The originally colorless catalyst turned purple after this treatment. The spectrum shows bands in the hydroxyl stretch vibration region at ca. 3500 and at 3640 cm^{-1} and in regions diagnostic for hydrocarbon vibrations, viz, bands at 2981, ca. 2940, ca. 2885, 1380, and ca. 1460 cm^{-1} . The hydroxyl bands are caused by associatively and dissociatively adsorbed water. This can be concluded from a comparison of this spectrum with a spectrum of adsorbed water (1).

The production of water by contact of alkenes with the catalyst proves that the catalyst is reduced by these alkenes.

The bands at 2981, ca. 2940, ca. 2885, 1380, and ca. 1460 cm^{-1} can be assigned according to well-known correlations between C-H vibration frequencies and hydrocarbon groups (3, 4):

- 2981 cm^{-1} : asymmetric CH stretch vibration in a methyl group
- ca. 2940 cm^{-1} : asymmetric CH stretch vibration in a methylene group
- ca. 2885 cm^{-1} : symmetric CH stretch vibration in a methyl group
- ca. 1460 cm^{-1} : asymmetric CH₃ deformation vibration in a methyl group and in a CH₂ group
- ca. 1380 cm^{-1} : symmetric CH₃ deformation vibration in a methyl group.

The relatively intense CH₃ band (2981 cm^{-1}) indicates presence of mainly methyl groups as opposed to methylene groups. The band at 1380 cm^{-1} suggests that these

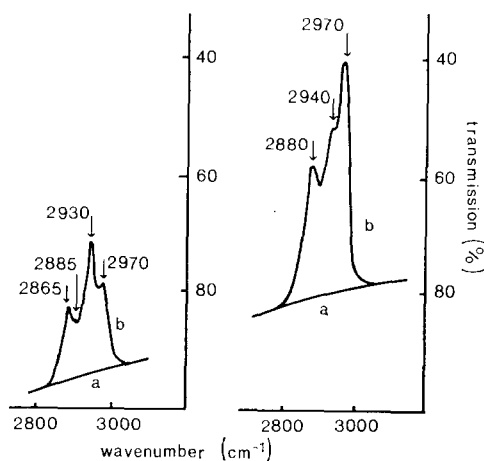


FIG. 2. Irreversible adsorption of ethene and butene-2 on Al₂O₃. (a) Before adsorption; and (b) after exposing the sample to ethene (right) and butene-2 (left) for 16 hr at ambient temperatures. Gaseous reactants have been pumped off. The sample was pretreated with oxygen at 823 K for 1 hr and then pumped off for 1 hr at the same temperature.

methyl groups are bonded to carbon atoms (4).

It is noted that the wavenumber values of the observed CH stretch vibrations are rather high. This might be caused by bonding of these methyl groups to oxidized hydrocarbon fragments, e.g., carboxyls, aldehydes, or condensed hydrocarbon fragments.

As expected, butene and pentene are also capable of reducing the catalyst at ambient temperatures. Ethene, however, behaves differently. Only after a much longer reaction time (48 hr) and at relatively high pressures (52×10^3 Pa) could some reduction be detected. This explains why Lin *et al.* (20) did not observe irreversible adsorption of ethene on an oxidized Re₂O₇/Al₂O₃ catalyst.

2. Irreversible Adsorption of Alkenes on Al₂O₃

For comparison, adsorption of ethene and butene on the carrier Al₂O₃ was studied. The carrier was pretreated in the same way as the catalyst. The spectra in Fig. 2 show the region of C-H stretch

TABLE 1
 C_2H_4/C_2D_4 Metathesis over Re_2O_7/Al_2O_3
 at Ambient Temperature^a

Time of exposure to propene (hr)	Conversion (%) after (hr):	
	0.5	1
0	0	0.5
0.5	5	11
1.5	10	19

^a Total pressure of C_2H_4 and $C_2D_4 = 465$ Pa. Conversion based on the amount of one of the starting materials.

vibrations of irreversibly adsorbed ethene and butene. In both cases the Al_2O_3 had been contacted with the alkene at ambient temperature for 16 hr. The butene studied was *cis*-butene-2 with initial pressure of 5.6×10^2 Pa.

After introducing the butene into the cell isomerization was found immediately, in agreement with the results of Peri (5). The spectrum of irreversibly adsorbed ethene shows bands at 2970, 2940, and 2880 cm^{-1} , in agreement with literature data (6, 7). These bands have been assigned to ethyl groups formed by self-hydrogenation (6, 7). The bands caused by adsorbed butene indicate also methylene (2930 and 2865 cm^{-1}) and methyl groups (2970 and 2885 cm^{-1}). From the relatively high intensity of the methylene bands it can be concluded that the latter groups are more abundant than the methyl groups. These results are completely different from those of the Re_2O_7/Al_2O_3 experiments, which agrees with the observation that the carrier is completely covered with Re_2O_7 (1).

3. The Activity for Metathesis

An elegant way to establish the activity of our Re_2O_7/Al_2O_3 metathesis catalyst is to follow the course of reaction of C_2H_4 with C_2D_4 giving asymmetric $C_2H_2D_2$. Ethene does not reduce the catalyst and double-bond shift reactions cannot interfere

as is the case in the metathesis of higher alkenes.

The production of asymmetric $C_2H_2D_2$ was monitored by measuring the intensity of the ν_7 [notation of Herzberg (8)] band at 751 cm^{-1} of asymmetric $C_2H_2D_2$: the reactant mixture was a 1:1 mixture of C_2H_4 and C_2D_4 . The activity at ambient temperatures was measured as a function of the extent of reduction of the catalyst by propene as measured by the time of exposure. Before the C_2H_4/C_2D_4 mixture was introduced, the fresh catalyst was exposed to propene (133×10^2 Pa) for specific periods at ambient temperatures and then pumped for 1 hr. Results of a typical experiment are given in Table 1.

The important conclusion can be drawn that active sites are only present after this reduction.

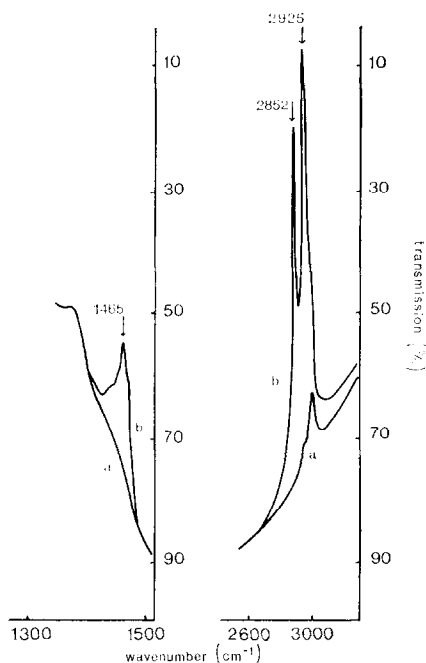


FIG. 3. Polymerization of ethene on a Re_2O_7/Al_2O_3 catalyst. (a) Spectrum of a catalyst reduced with butene-2 at ambient temperature. (b) After exposing the catalyst to ethene (65×10^2 Pa) for 72 hr at ambient temperature. Gaseous reactants have been pumped off.

It is very interesting that a catalyst reduced with CO or NH₃ at temperatures above 573 K had no appreciable activity. Activity, however, was found for the H-D exchange reaction between C₂H₄ and C₂D₄ (C₂HD₃, C₂H₃D, and *cis*- and *trans*-C₂H₂D₂ were detected through their specific infrared bands).

4. Polymerization of Ethene on Re₂O₇/Al₂O₃

Figure 3 shows the infrared spectra of a Re₂O₇/Al₂O₃ catalyst reduced initially by *cis*-butene-2 and subsequently by exposure for 72 hr to ethene at 65 × 10³ Pa and ambient temperature.

Spectra are recorded after pumping away the gaseous reactants. In the spectrum of the catalyst exposed to ethene, three bands are observed, namely, two sharp intense ones at 2925 and 2852 cm⁻¹ and a medium band at 1465 cm⁻¹. According to well-known correlations they can be assigned to methylene groups. Bands which might be caused by methyl groups are not observed: apparently linear long-chain polyethene had been formed. This polyethene was also observed visually: the original transparent catalyst turned opaque on prolonged exposure to ethene. Under the conditions in which the metathesis activity was determined, namely, by following the reaction of C₂H₄ with C₂D₄ at a total pressure 13 × 10² Pa, ambient temperature and a maximum reaction time 16 hr, polymerization of the reactants has never been observed.

5. Adsorption of NO and CO

Adsorption of NO did not occur on a fresh catalyst at ambient temperatures. However, after reduction adsorption occurs.

Figure 4 shows the spectra of NO adsorbed at ambient temperature on two catalysts differing in Re₂O₇ content. Both catalysts were reduced by butene-2. Spectra were recorded 1 hr after contacting the catalyst with NO. Longer exposure on

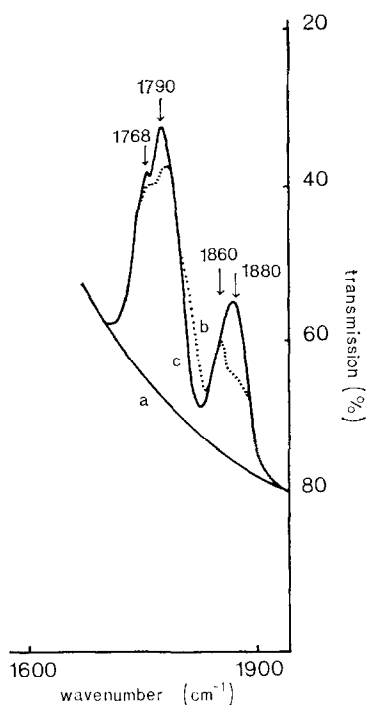


FIG. 4. Adsorption of NO on a catalyst reduced with alkenes at ambient temperatures. (a) Before adsorption; (b) and (c) NO adsorbed on a catalyst with Re contents of 19 and 25%, respectively.

evacuating for 1 hr did not result in different spectra. Both spectra are similar in their bands at 1768 and 1790 cm⁻¹, while between 1800 and 1900 cm⁻¹ there are differences. At the 25% Re₂O₇ catalyst one band is observed at 1880 cm⁻¹, while the other spectrum shows a band at 1860 cm⁻¹ with a shoulder at 1890 cm⁻¹. Close inspection of the 1880 cm⁻¹ band might suggest that it is composed of the two bands at 1860 and 1890 cm⁻¹ shown in the spectrum of the 19% Re₂O₇ catalyst.

The bands are all in the region diagnostic for N-O stretch vibrations of π -bonded NO molecules: Me-N-O (9). As for such bonding *d* electrons are a prerequisite the NO molecules must be bonded to the partially oxidized Re ions generated by the reduction of the catalyst. By volumetric adsorption attempts were made to measure the amount of adsorbed NO as a function

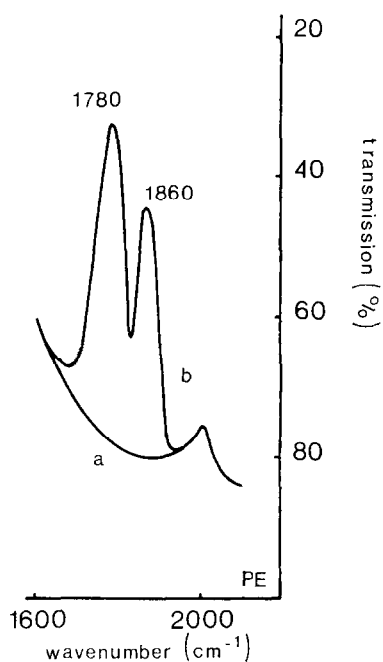


Fig. 5. Adsorption of NO on a catalyst reduced with NH_3 (1). (a) Before adsorption; and (b) after adsorption of NO at ambient temperatures.

of the extent of reduction by propene. However, the amount of adsorbed NO was below the detection limit of the adsorption apparatus.

Its sensitivity corresponded with one NO per 10^4 \AA^2 surface area. From this value, the Re_2O_7 content and the catalyst surface area it follows that the upper limit of the amount of active ions corresponds with 0.3% of the total amount of Re atoms.

It is interesting to compare this NO adsorption with NO adsorption on a catalyst reduced at higher temperatures (573 K) with CO or NH_3 (1). The spectrum of NO adsorbed on a catalyst reduced with NH_3 is shown in Fig. 5 (NO on a catalyst reduced with CO gives an identical spectrum). NO adsorption in this case is also fast and on pumping at ambient temperatures desorption of NO was not observed. The effect of reduction conditions on the nature of the surface is demonstrated by the difference in NO adsorption as shown by the spectra in Figs. 4 and 5. NO proved to be a

poison for the H-D exchange activity of the catalyst which was reduced at high temperatures. Adsorption of CO (13×10^3 Pa, ambient temperatures, 16 hr) on an unreduced catalyst or on room-temperature-reduced catalysts has never been observed.

6. Isomerization of Alkenes on $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$

On reduction of $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ with alkenes water is liberated, which at ambient temperatures remains for the greater part associatively adsorbed on the catalyst surface. This water has certain properties which are important with respect to the nature of the isomerization activity of this

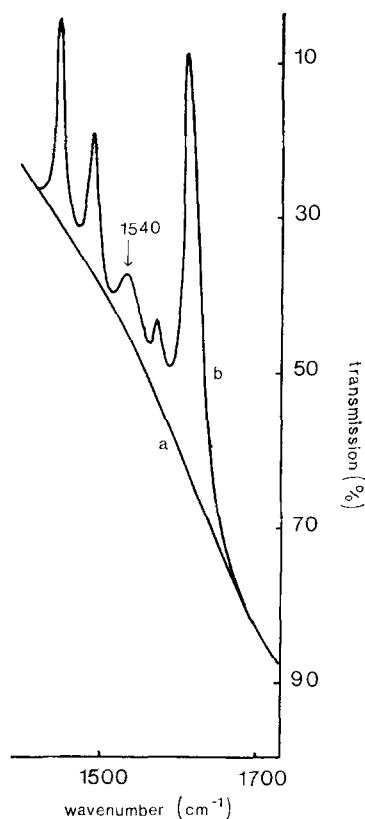


Fig. 6. Brønsted acidity of associatively adsorbed water. (a) Spectrum after reduction with alkenes; (b) after adsorption of pyridine at ambient temperatures with catalyst exposed to pyridine vapor, followed by pumping for 0.5 hr at ambient temperatures.

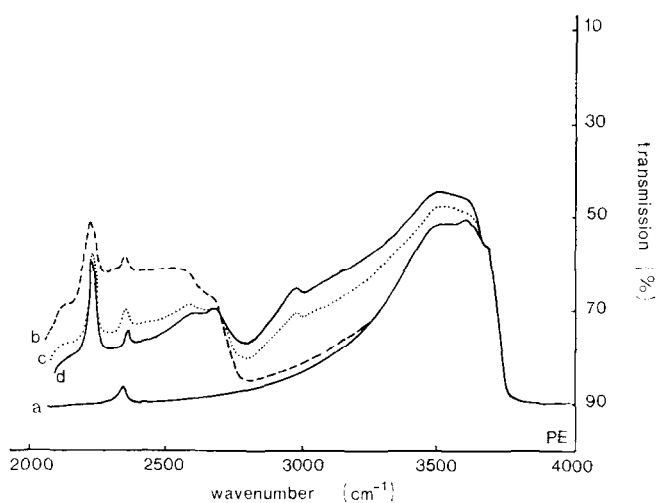


FIG. 7. H-D exchange between alkenes and associatively adsorbed D₂O, which is liberated on reduction of the catalyst by deuterated alkenes. (a) Fresh catalyst; (b) after reduction with per-deutero-butene-2 at ambient temperatures; (c) 1.5 hr after exposing the catalyst to propene (40×10^2 Pa) at ambient temperatures; and (d) after 3.5 hr.

catalyst. In the first place it generates Brønsted acidity, as is shown by the result of the following experiment.

A catalyst, reduced with butene-2 (65×10^2 Pa, ambient temperature, 4 hr) was contacted with a small amount of pyridine. The infrared spectrum of the adsorbed pyridine is shown in Fig. 6. Among others a band is visible at 1540 cm^{-1} , which indicates the presence of pyridinium ions (10). This 1540 cm^{-1} band is absent in the spectrum of pyridine adsorbed under the same circumstances on an unreduced catalyst. Pyridine adsorbed on a fresh catalyst on which small amounts of water adsorbed at ambient temperatures are present, is also protonated. As perrhenic acid is a strong acid, protonation is obviously to be expected.

A second property of associatively adsorbed water, either formed by reduction or directly adsorbed on a fresh catalyst, is its capability to exchange its hydrogen with hydrogen of propene, butene, etc. A typical experiment was as follows: A Re₂O₇/Al₂O₃ catalyst was reduced with C₄D₈ (52×10^2 Pa, ambient temperature, 16 hr). Propene (40×10^2 Pa) was intro-

duced into the cell. After 1.5 hr the greater part of the associatively adsorbed D₂O had disappeared while associatively adsorbed H₂O had been formed (Fig. 7). Reduction of the catalyst by propene is too slow to account solely for the production of water; therefore H-D exchange between the primary-formed associatively adsorbed D₂O with propene must have occurred.

7. Active Sites and Reaction intermediates

Simultaneously with the generation of metathesis activity by reduction with propene or butene, methyl and (less numerous) methylene groups are formed. It might therefore be possible that these groups are somehow part of the active sites and involved in the course of reaction. To verify this possibility propene was contacted with a catalyst reduced with butene-*d*₈. While the propene was quickly converted to ethene and butene a change in the -CD₃ and -CD₂ infrared bands, which would suggest the importance of these groups with respect to the reaction mechanism, was not observed. It is also important to note that influence of ad-

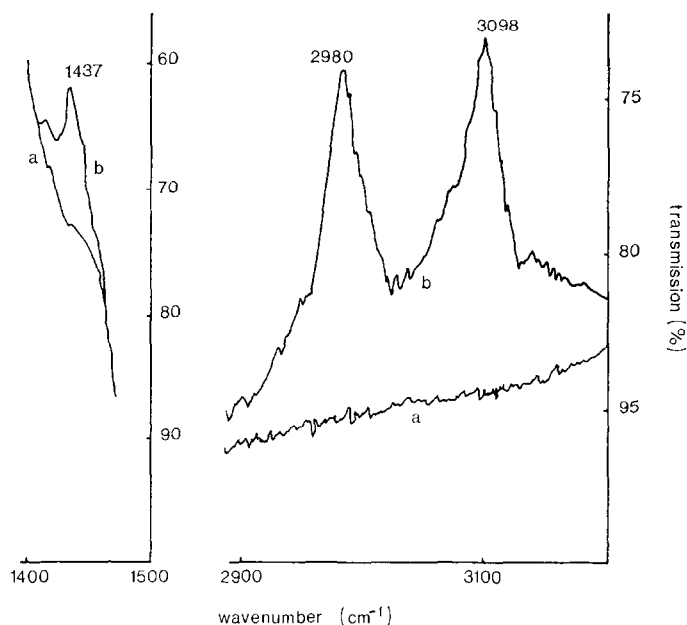


FIG. 8. Reversible adsorption of ethene on active $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst at ambient temperatures. (a) Before and after exposure of the catalyst to ethene. (b) Catalyst exposed to ethene at 55×10^3 Pa (this spectrum was taken with reduced source intensity).

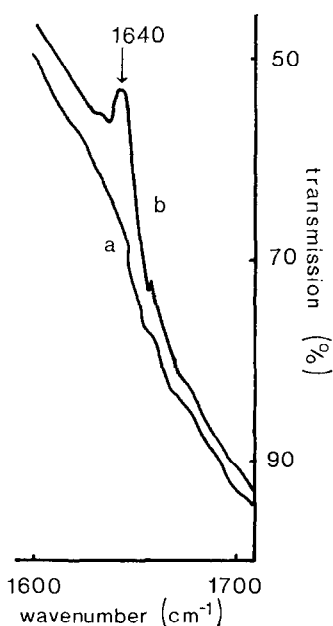


FIG. 9. Reversible adsorption of propene on an active $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst. (a) Before and after adsorption. (b) Catalyst exposed to a mixture of ethene (30×10^3 Pa) and propene (10×10^3 Pa) (this spectrum was taken with reduced source intensity).

sorbed NO, a poison for the metathesis reaction, on the shape and position of these methyl and methylene bands has never been observed. Apparently, these groups are not relevant for insight into the reaction mechanism. Several attempts have been made to observe alkenes adsorbed on the active sites of a working catalyst. Figure 8 is a typical example of a spectrum of ethene adsorbed on a highly active catalyst, which has been reduced with butene- d_3 . The activity, as determined by following the reaction of C_2H_4 with C_2D_4 , did not differ before and after the adsorption of ethene. The spectrum is not different from that of ethene adsorbed under the same circumstances on a nonreduced or NO-poisoned catalyst. As this spectrum is also virtually identical with the spectrum of ethene reversibly adsorbed on Al_2O_3 , it must be caused by ethene adsorbed in a nonspecific way. We assign the bands at 3098, 2980, and 1436 cm^{-1} to ν_9 , ν_{11} , and ν_{12} [notation of Herzberg (8)] of ethene

whose structure is not affected by the adsorption.

In other experiments the adsorption of mixtures of propene and ethene was studied. When the ethene present is in a sufficient excess over the amount of propene the composition of the mixture will virtually not change during the time necessary to record the spectrum and one is able to measure the frequency of the relatively intense C=C stretch vibration of propene which is sensitive to π -complex formation (12). A band, caused by loosely adsorbed propene (on pumping it desorbs immediately) was found at 1640 cm⁻¹ (Fig. 9). This band, however, is also present in the spectrum of propene adsorbed on Al₂O₃ (13) and we assign the band therefore to a C=C stretch vibration of a very loosely nonspecifically adsorbed propene [the frequency of this vibration in gaseous propene is 1647 cm⁻¹ (8)].

DISCUSSION

The Re₂O₇/Al₂O₃ catalyst is comparable with MoO₃/Al₂O₃ in a number of respects. In Part I (1) the monolayer structure of both catalysts was pointed out. The results of this work show a similarity in catalytic properties. In addition to being metathesis catalysts both develop activity only on reduction: the active centers contain partly oxidized transition metal ions. For the Re₂O₇/Al₂O₃ catalyst this is proved by the results of our experiments with C₂H₄/C₂D₄ mixtures. The beneficial effect of reduction of MoO₃/Al₂O₃ on the metathesis activity is indicated by other authors (14, 15). With respect to the manner in which reduction leads to activity, Re₂O₇/Al₂O₃ is different from MoO₃/Al₂O₃ as reduction at higher temperature does not result in activity for metathesis. In contrast, high-temperature reduction of MoO₃/Al₂O₃ leads to higher activity than reduction at low temperatures (14, 15). As far as NO adsorption is a sound characterization of the surface the results of the NO adsorption experiments also

show the effect of the reduction conditions on the properties of the reduced catalyst. The difference in behavior of Re₂O₇/Al₂O₃ and MoO₃/Al₂O₃ in this respect may probably be related to the difference in their reduction properties (1): Re₂O₇ on Al₂O₃ can, at least partly, be reduced to the corresponding metal (H₂, 773 K), while this is not possible for MoO₃ on Al₂O₃.

A second common property of the two catalysts is that both are catalysts for the polymerization of ethene, producing linear polyethene. It is well known that MoO₃/Al₂O₃ catalysts catalyze the polymerization of ethene (16), but polymerization activity of the Re₂O₇/Al₂O₃ catalyst has not been reported as far as we know. However, the activity is so low that Re₂O₇/Al₂O₃ as a polymerization catalyst only seems interesting for theoretical reasons. It is interesting that a number of different metathesis catalysts, such as MoO₃/Al₂O₃, WCl₆/Bu₄Sn (18), and MoCl₅/Bu₅Sn (19), also polymerize ethene to linear polyethene, which may suggest a relationship in the mechanism of metathesis and polymerization reactions. The results of our NO adsorption experiments show that the surface density of the metathesis sites is small, a property which has also been found for another important metathesis catalyst, WO₃/SiO₂ (17). The low site density may be the reason why no reaction intermediates have been detected.

NO adsorbs only on a reduced catalyst. It was already suggested that NO is π -bonded to the partially oxidized Re ions of which some are the catalytically active ones. This may indicate that one step in the metathesis reaction mechanism is π -complex formation of the alkenes with the Re cation.

The isomerization activity of our catalyst is at least partly accounted for by associatively adsorbed water, which generates acidity. It showed its acidity by protonating pyridine and by being able to exchange hydrogen with alkenes. It can

be envisaged that exchange of hydrogen between the water and alkene proceeds via a carbonium ion and that in this process a double-bond shift occurs.

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