The Surface Acidity of Pure and Modified Aluminas in Re/Al$_2$O$_3$ Metathesis Catalysts as Studied by ^{1}H MAS NMR Spectroscopy and Its Importance in the Ethenolysis of 1,5-Cyclooctadiene

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In this work some very active low-loading metathesis catalysts are presented in which rhenium is directed to favourable sites on the surface of γ-alumina. This was achieved by ion exchange of Cl$^-$, F$^-$, MoO$_4^{2-}$, and some carboxylic acid anions on the surface prior to rhenium adsorption or by ion exchange of very small amounts of ReO$_4^-$ (around 0.08 Re atoms/nm^2). The results of catalyst tests for the ethenolysis of 1,5-cyclooctadiene are presented and the catalysts are characterised by solid state ^{1}H MAS NMR spectroscopy. Two distinct peaks are observed in ^{1}H MAS NMR spectra of dehydrated γ-alumina and the catalysts. The peaks are assigned to the more basic and more acidic OH groups. They are used to describe the bonding of ion-exchanged anions to the surface. © 1994 Academic Press, Inc.

INTRODUCTION

From an industrial point of view, olefin metathesis reactions are very attractive for many reasons (1, 2). They offer a chance to produce useful compounds which cannot be synthesized from readily available starting materials by standard methods of organic chemistry (3). These include nonconjugated terminal olefins which can be prepared from ethene and commercially available cyclic olefins such as 1,5-cyclooctadiene (COD). Since the activation energy is low, the reactions can often be run under mild conditions and so the possibility for side reactions such as isomerization is low and the processes are safer.

The methathesis reaction mechanism is now generally accepted to proceed via a carbene (metal alkylidene or metallaolefin) complex (1). The use of poisonous cocatalysts such as aluminum, tin or lead alkyls can be avoided if the metal is active enough to form carbene with feed olefins. The details of the carbene formation are not clear but many possible routes have been proposed (4, 5).

The support has long been recognized to have a significant role in the structure and activity of heterogeneous rhenium-based metathesis catalysts (6–9). It is evident th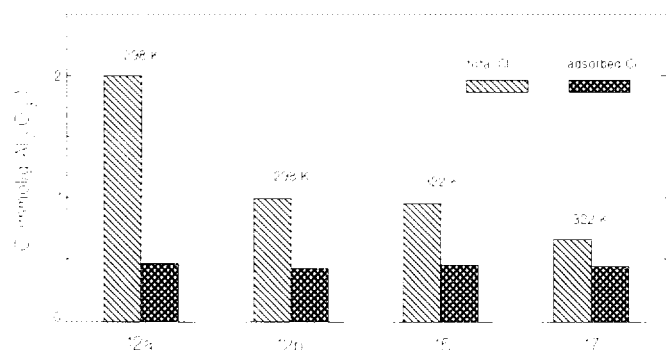at the final catalyst performance can be significantly influenced during the first phase of the catalyst preparation, when the metal is introduced onto the surface of the support. When preparing Re/Al$_2$O$_3$ catalysts it is possible to maximise the electron deficiency on Re, and metathesis activity, by situating ReO$_4^-$ at the most electron deficient, i.e., acidic, sites (10). It is known that electron deficiency in well defined homogeneous metathesis catalysts correlates with activity (11, 12).

Experience has shown that the use of mineral acids in the preparation of metathesis catalysts enhances the activity (13, 14). The presence of oxides such as V$_2$O$_5$, WO$_3$, MoO$_3$, and B$_2$O$_3$ on alumina has been shown to increase metathesis activity of Re (15–18) and a positive correlation with the Brønsted acidity of these modified catalysts and the metathesis activity has been found (18, 19).

A surface model of γ-alumina has been given by Knözinger and Ratnasamy (20). It proposes five different types of surface hydroxyls depending on their coordination to either tetrahedral or octahedral aluminium or as bridged species between different combinations of these. Most investigations to date have used FT-IR spectroscopy to characterise the alumina surface before and after the adsorption of the surface species (10, 21, 22). It can distinguish five different OH groups on the surface of γ-alumina (23) but the spectra are not quantitative in a straightforward way. In some cases solid state NMR spectroscopy can be used to probe the surface when the adsorbed probe molecules are magnetically active (24) and ^{27}Al MAS NMR has been used to investigate the surface of the pure alumina directly (25). However, both these techniques are rather time-consuming and can also be difficult to interpret. ^{1}H MAS NMR can give information concerning the OH groups on the surface of aluminas and silica-aluminas (26) but under normal drying conditions pure alumina gives a broad featureless resonance from which it is difficult to extract any useful information.

In this paper we present some very active metathesis catalysts in which rhenium is directed to favourable sites

FIG. 1. Chloride adsorption of γ-alumina under various conditions. The samples were prepared using 0.10 M HCl (samples 12a, 12b, and 15) or 0.20 M HCl (sample 17).

on the surface of γ-alumina. The results of catalyst tests for the ethenolysis of COD are presented and some calcined samples are characterised by solid state ^{1}H MAS NMR.

METHODS

Catalyst Preparation

The catalysts were prepared by adsorption from an excess of solution (ion exchange) or in some examples by dry impregnation. In the former method the support was immersed in an aqueous solution containing the compound to be adsorbed (solution (ml)/support (g) 3–30). In acidic solution the following reactions take place:

$$Al-OH + H^+ \rightleftharpoons Al-OH_2^+ \quad [1]$$

$$Al-OH_2^+ + X^- \rightleftharpoons Al-X + H_2O. \quad [2]$$
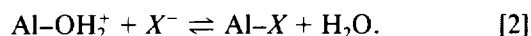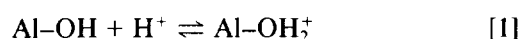
The solution was left to stand in a closed vessel (at room temperature unless otherwise mentioned) and shaken occasionally. The total reaction time was always more than 15 h to ensure that the system had reached equilibrium. After the reaction the material was filtered and washed three times with an excess of water. The process was repeated with another solution if desired and then dried at 393 K. If the adsorption process is not very sensitive to changes in pH or ion strength, the result is independent of the amount of the anion in the solution within a certain range (Fig. 1).

In dry impregnation only a sufficient amount of solution was used so that the particles started to stick together (solution (ml)/support (g) 0.7–1). After impregnation the samples were not washed out but only dried at 393 K.

The material was calcined in a steel tube at 880 K for 3 h in air (WHSV 1–6 h^{-1}) and 0.5 h in nitrogen (WHSV 1–6 h^{-1}) and then cooled to room temperature under nitrogen flow. The temperature was measured with a thermocouple which was in a pocket inside the tube.

The details of the preparation of each sample are given in Table 1.

Test Reaction

The most probable reaction mechanism for the metathesis of COD and ethene using a heterogeneous catalyst without a cocatalyst (4, 27) is presented in Figs. 2 and 3.

Coordination of the cyclooctadiene ring leads to the formation of the initial carbene I which can react with ethene or another molecule of COD. Because the ring opening means release of ring strain (28), this last alternative is favoured. It leads to the formation of carbene II.

TABLE 1

Preparation of the Samples

Sample	Preparation method[d]	Solutions	Solution (ml)/ support (g)	X^c (%)	Re (%)
1	a	0.005 M HReO₄	4.0	—	0.33
2	a	0.005 M HReO₄	4.0	—	0.39
3	a	0.008 M HReO₄	4.0	—	0.48
4	a	0.01 M HReO₄	4.0	—	0.64
5	i	0.075 M HReO₄	0.8	—	1.4
6	a	0.020 M HReO₄	4.0	—	1.5
7	a	0.050 M HReO₄	2.4	—	2.0
8	a	0.05 M HReO₄	4.0	—	3.0
9	a	0.10 M HReO₄	4.0	—	5.3
10	a	0.20 M HReO₄	4.0	—	6.8
11	i	0.88 M HReO₄	1.0	—	14.1
12a	a	0.10 M HCl	20	1.6 (Cl)	—
12b	a	0.10 M HCl	10	1.5 (Cl)	—
13	a	0.10 M HCl 0.020 M HReO₄	30 3.0	0.70 (Cl)	0.80
14	a	0.10 M HCl 0.050 M HReO₄	10 4.0	0.65 (Cl)	1.8
15	a	0.10 M HCl[a] 0.050 M HReO₄[a]	9.5 3.8	0.80 (Cl)	2.0
16	a	0.10 M HCl 0.050 M HReO₄	10 4.0	0.76 (Cl)	2.1
17	a	0.20 M HCl[a] 0.060 M HReO₄[a]	3.3 3.3	0.75 (Cl)	2.2
18	a	0.10 M HCl 0.050 M HReO₄	8.3 4.0	0.74 (Cl)	2.3
19	a	0.11 M HF	5.0	0.68 (F)	—
20	a	0.46 M HF 0.050 M HReO₄	10 4.0	3.5 (F)	0.90
21	a	0.091 M HF 0.050 M HReO₄	8.3 4.0	0.92 (F)	2.4
22	a	0.11 M HF 0.050 M HReO₄	5.0 4.0	1.1 (F)	2.9
23	a	0.10 M (NH₄)₂MoO₄[b]	6.0	3.8 (Mo)	—
24	a	0.14 M (NH₄)₂MoO₄[b] 0.058 M HReO₄ 0.10 M	3.0 3.0	3.7 (Mo)	1.3
25	a	(NH₄)₂MoO₄[b] 0.050 M HReO₄	6.0 4.0	4.0 (Mo)	1.6
26	i	0.54 M (NH₄)₂MoO₄ 0.22 M HReO₄	0.8 0.8	4.9 (Mo)	3.4
27	a	0.10 M (COOH)₂ 0.020 M HReO₄	15 3.0	—[c]	0.18
28	a	0.1 M citric acid 0.020 M HReO₄	15 3.0	—[c]	0.29

[a] At 322 K.
[b] 0.5 M acetate buffer, pH 5.
[c] Not measured.
[d] a = adsorption with ion exchange. i = impregnation.
[e] The amount of the given element calculated from the elemental analysis.
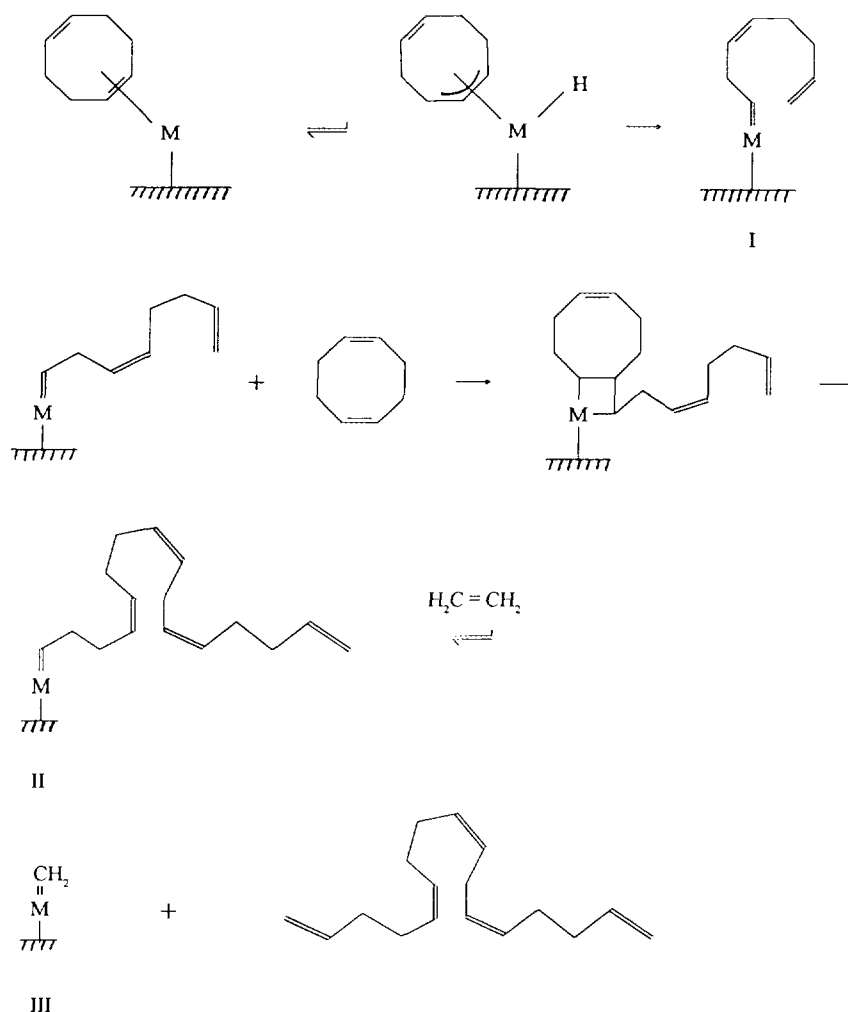
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FIG. 2. The mechanism of activation in ethenolysis of 1,5-cyclooctadiene. In this case M is Re (oxo ligands omitted).

The reaction with ethene forms carbene III which is the active propagation species.

Successive reactions with COD give carbenes IV. The carbon chains are released and carbene III is restored by the reaction with ethene. Any of the double bonds in the carbon chains can react further with carbene III and ethene. When the internal double bond in C_{10} (1,5,9-decatriene) reacts, C_6 (1, 5-hexadiene) is formed.

The activated catalyst and the reaction mixture containing 70% toluene, 20% COD, and 10% heptane (standard for gas chromatography) were loaded into a batch reactor in a dry box under a nitrogen atmosphere (3–5 ppm O_2). A COD (g)/catalyst (g) ratio of 50 was used. The reactor was connected to an ethene line and the mixing was started. The pressure was kept at 20 bar during the reaction. No external heating was applied. If the catalyst was active, the temperature increased quickly by a few degrees, up to 302 K. The reaction mixture was sam-

pled by opening a valve for a few seconds. The samples were analyzed by temperature programmed gas chromatography using a J & W column DB-1, FID detector and helium as carrier. The integrated peak areas were corrected using standard solutions.

Detailed analysis of the reaction kinetics would be extremely complicated as can be seen in Fig. 3. To obtain a simple semiquantitative idea of the catalyst activity, we measured the amount of 1,5-hexadiene formed (mol) per rhenium (mmol):

$$C_6 \text{ (mol/mmol)} = [C_6 (\%) \times \text{ref (g)}] / [\text{ref} (\%) \times M (C_6) \times \text{Re (mmol)}], \quad [3]$$

where C_6 (%) = 1,5-hexadiene (%) in the solution based on the corrected peak area, ref (g) = heptane (g), ref(%) = heptane (%) in the solution based on the corrected
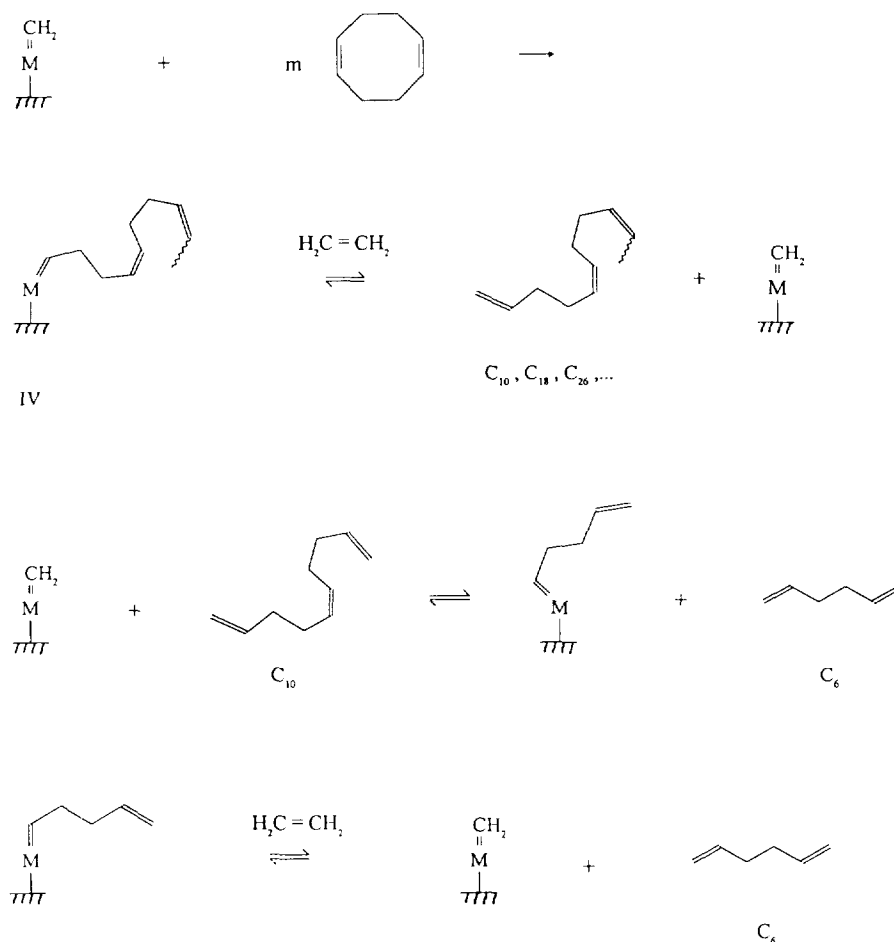
FIG. 3. The mechanism of 1,5-hexadiene formation in ethenolysis of 1,5-cyclooctadiene. M is Re (oxo ligands omitted).

peak area, M (C₆) = molar mass of 1,5-hexadiene (g/mol), Re (mmol) = rhenium (mmol) in the calcined catalyst.

The measurements were carried out after 2 h of contact with ethene. After an initiation time of about 10 min (formation of carbenes, ring opening of COD) the formation of hexadiene takes place at an almost constant rate.

Elemental Analyses

Rhenium and molybdenum were determined by x-ray fluorescence. For other element determinations the catalyst was decomposed in sulphuric acid solution. Chlorine was determined by potentiometric titration with AgNO₃ and fluorine with an ion selective electrode.

¹H NMR Measurements

After heat treatments all samples were handled inertly. When samples were not calcined, they were heat-treated under vacuum at 450 K for 12 h before the NMR experiments to remove the physically adsorbed water. The

NMR experiments were carried out using a JEOL GSX270 instrument with a homebuilt low ¹H background double bearing MAS probe. The samples were loaded into 7 mm o.d. zirconia rotors in a dry nitrogen atmosphere and were rotated at speeds of around 6.5 kHz using nitrogen gas. A 45 degree excitation pulse of 2 μs was used with a recycle delay of 10 s and 100 transients were acquired. The small residual ¹H background signal which was obtained from an empty spinning rotor was subtracted from all spectra. Although ¹H MAS NMR cannot resolve all the Al–OH groups present, it is possible to obtain more quantitative information than with IR concerning the total number of OH groups present on the surface. This was carried out by comparing the signal intensities of a known weight of sample with untreated silica (EP10 from Crosfield) with a OH group density of 19.5 × 10²⁰ OH/g. An increase in the recycle delay from 10 to 20 s had no effect on the intensity of the signal for the 880 K calcined sample and we conclude that the NMR measurements are quantitative. Occasional measurements of the surface areas of the catalysts have shown that the catalyst preparation

TABLE 2

Summary of the ¹H MAS NMR Experiments

Sample	OH/nm²	Loss of OH/nm²	X^b/nm²	ΔOH/X	Y^b/nm²	ΔOH/Y
Support[a]	8.2	—	—	—	—	—
Support	2.1	—	—	—	—	—
5	1.4	0.7	0.3 Re	2.3	—	—
6	1.3	0.8	0.3 Re	2.7	—	—
7	1.3	0.8	0.4 Re	2.0	—	—
9	1.0	1.1	0.9 Re	1.2	—	—
10[a]	8.0	-0.2	1.4 Re	-0.1	—	—
10	1.2	0.9	1.2 Re	0.8	—	—
12a	1.3	0.8	0.9 Cl	0.9	—	—
16	0.8	1.3	0.9 Cl	1.0	0.4 Re	1.0
18	1.0	1.1	0.6 Cl	1.0	0.4 Re	1.0
19	1.0	1.1	1.2 F	0.9	—	—
23[a]	10.6	-2.4	1.3 Mo	-1.8	—	—
23	1.0	1.1	1.3 Mo	0.8	—	—
25	0.7	1.4	1.3 Mo	0.8	0.3 Re	1.0

[a] Not calcined; heat treatment under vacuum at 453 K for 12 h.

[b] The surface concentration of the given element calculated from the elemental analysis.

does not have a significant effect on the surface area of the pure γ-alumina.

It has been suggested that ¹H NMR does not see all the NMR signal due to the possible presence of an Al nucleus with a large quadrupole interaction nearby (29). However, as shown by IR (10) and NMR (30) studies, the surface aluminium atoms are not in environments which would give rise to large electric field gradients. In any event it is unlikely that the T_1 of the Al nucleus is so short that it broadens the ¹H line substantially since the Al–¹H dipolar interaction is so weak and the Al T_1 is of the order of milliseconds (31).

The NMR results for the samples examined here are shown in Table 2.

Materials

Perrhenic acid (Hermann C, Starck Berlin, 7.2 *M*, 99.99%), ammonium molybdate (VI) (99.99%, Aldrich), hydrochloric acid (FF-Chemicals, standard solution, 0.1 *N*), hydrofluoric acid (Riedel-de-Haen, 40%), oxalic acid dihydrate (99+%, J. T. Baker) and citrate buffer (FF-Chemicals, pH 4 standard) were used as received. Acetate buffer was prepared from acetic acid (99–100%, J. T. Baker) and potassium acetate (99+%, J. T. Baker). Deionized water was used for the catalyst preparation. The support was Akzo 000–1.5E γ-alumina ground to particle size 0.5–1.0 mm, (S_{BET} 190 m²/g, average pore diameter 10 nm).

Toluene (Merck, p.a.) was distilled over sodium and heptane (Merck, p.a.) over P_2O_5 under nitrogen atmosphere but 1,5-cyclooctadiene (Aldrich, 99+ %, sealed

under nitrogen) was used as received. The reaction solutions were prepared in a dry box and kept over molecular sieves before use. Ethene (AGA, 99.95%), synthetic air (Messer Griesheim) and nitrogen (AGA, 99.999%) were fed through a tube containing copper(II) oxide catalyst (BASF) or through Messer Griesheim Oxysorb and dried with molecular sieves or Messer Griesheim Hydrosorb.

RESULTS

Support

An example of the ¹H MAS NMR spectra of γ-alumina at 298 K after calcination at various temperatures is shown in Fig. 4. Since some of the NMR intensity of the signal resides in the spinning sideband manifold, the areas of these should also be taken into account in order to obtain a correct measurement for the number of OH groups present. As can be seen from the spectra, the intensity of these decrease with increasing calcination temperature and is due to the reduction in the dipolar interaction between the ¹H nuclei as the OH group population decreases. The values measured for the 450 and 880 K calcined samples are 8.2 and 2.1 OH/nm² respectively, in agreement with previous measurements on a range of aluminas (20). After calcination at 880 K, the ¹H MAS NMR spectrum exhibits two resonances at 0 and 2.5 ppm.

When Cl⁻ or F⁻ are adsorbed on alumina and the calcined sample is examined with ¹H MAS NMR, only the peak at 2.5 ppm is present (Figs. 5 and 6). Similar experiments using IR have been carried out and show that the bands assigned to the most basic OH groups disappear (32, 33). We conclude from this comparison that the peak
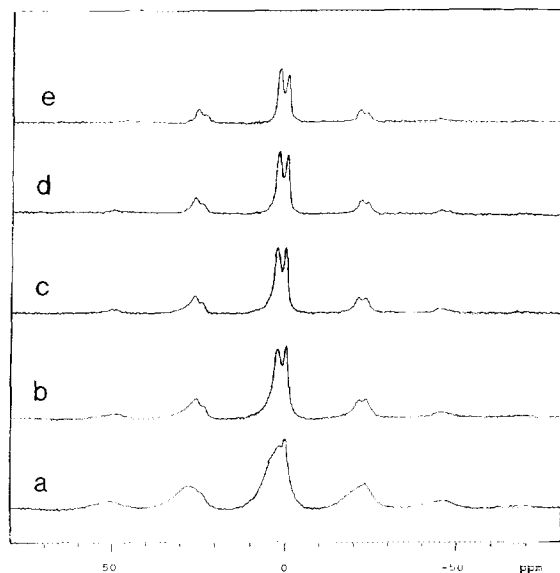

FIG. 4. ¹H MAS NMR spectra of γ-alumina at 298 K after calcination at (a) 470 K, (b) 620 K, (c) 720 K, (d) 770 K, and (e) 880 K.
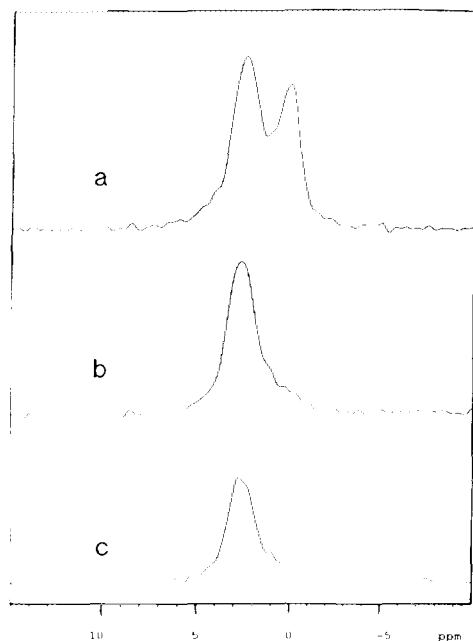
FIG. 5. ¹H MAS NMR spectra at 298 K of (a) γ-alumina, (b) Al₂O₃ + 1.6% Cl (sample 12a) and (c) Al₂ O₃ + 0.76% Cl + 2.1% Re (sample 16) calcined at 880 K.
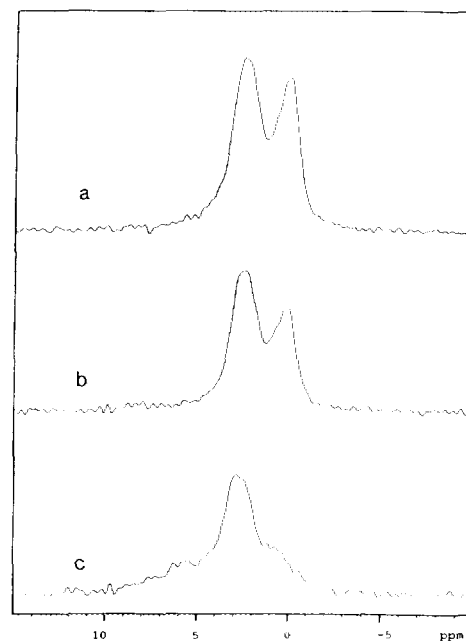

FIG. 7. ¹H MAS NMR spectra at 298 K of (a) γ-alumina, (b) Al₂O₃ + 1.5% Re (sample 6) and (c) Al₂O₃ + 6.8% Re (sample 10) calcined at 880 K.

at 0 ppm in the ¹H MAS NMR spectrum arises from these most basic OH groups while the peak at 2.5 ppm is due to the more acidic OH groups. While the resolution of the ¹H MAS NMR method is inferior to IR, the basic OH groups can be identified qualitatively and the total number of OH groups obtained quantitatively. Comparison of the number of lost OH groups with the number of adsorbed

FIG. 6. ¹H MAS NMR spectra at 298 K of (a) γ-alumina and (b) Al₂O₃ + 0.68% F (sample 19) calcined at 880 K.

anions ($\Delta OH/X$) can then give an idea about the bonding on the surface. For Cl⁻ and F⁻ the experimental value for $\Delta OH/X$ is 0.9, close to the value of 1 expected (Table 2).

Al₂O₃ + Re

Rhenate anion (ReO₄⁻) reacts with all the different types of OH groups present on the alumina surface. This is clearly seen in spectra a and b in Fig. 7 where the ¹H MAS NMR spectrum of alumina before and after adsorption of 1.5% Re is shown. Here both types of OH groups are reduced in intensity after adsorption but basic OH groups are reacted slightly more.

At higher Re loadings the ¹H MAS spectrum is somewhat different (spectrum c in Fig. 7) with more of the basic OH groups reacting and some evidence for the presence of another broader resonance around 5 ppm. At loadings >0.5 atoms/nm² every Re atom replaces one OH group but at lower loadings up to three OH groups are replaced by one Re atom (Table 2).

It is known that the activity of Re/A₂O₃ in propene metathesis (34) and ester metathesis (in the presence of Sn(CH₃)₄)) (35) decreases when the rhenium loading decreases from about 10%. However, we have found that the specific activity increases when the rhenium loading decreases from 0.90 Re/nm² (5.3% Re) to 0.082 Re/nm² (0.48% Re) if the COD/catalyst ratio is kept constant (Table 3 and Fig. 8).
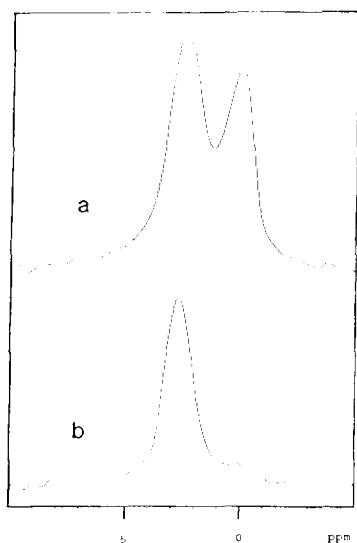
TABLE 3

Catalyst Performance

Sample	Re (nm^{-2})	X	X^b (nm^{-2})	COD conversion (%)	COD conversion (mol/ mmol Re)	C_6 (mol/ mmol Re)
1	0.056	—	—	7.9	2.1	0.05
2	0.066	—	—	11	2.4	0.06
3	0.082	—	—	42	7.3	0.54
4	0.11	—	—	39	5.0	0.45
6	0.26	—	—	36	2.1	0.27
8	0.51	—	—	35	1.0	0.17
9	0.90	—	—	42	0.69	0.09
11	2.40	—	—	43	0.26	0.06
13	0.13	Cl$^-$	0.63	55	6.2	1.2
14	0.31	Cl$^-$	0.58	76	3.6	1.3
15	0.34	Cl$^-$	0.72	70	3.0	1.3
16	0.36	Cl$^-$	0.68	85	3.3	1.4
17	0.37	Cl$^-$	0.67	75	2.9	1.3
18	0.39	Cl$^-$	0.66	79	3.0	1.1
20	0.15	F$^-$	5.84	52	4.6	0.90
21	0.41	F$^-$	2.00	79	2.8	1.0
22	0.49	F$^-$	1.83	86	2.4	1.3
23	—	MoO$_4^{2-}$	1.25	0	0	0
24	0.20	MoO$_4^{2-}$	1.22	75	5.3	1.3
25	0.27	MoO$_4^{2-}$	1.32	65	3.5	1.2
26	0.58	MoO$_4^{2-}$	1.62	69	1.7	0.59
27	0.031	(COO$^-$)$_2$	—^{a}	20	9.4	0.28
28	0.049	HOC(CH$_2$COO$^-$)$_2$COO$^-$	—^{a}	34	10	0.67

^{a} Not measured.

^{b} The surface concentration of Cl, F, or Mo calculated from the elemental analysis.

Al_2O_3 + Mo + Re

The ^{1}H MAS NMR spectrum of the alumina after treatment with $(NH_4)_2MoO_4$ suggests that molybdate anions are nonselective in their reaction with the different OH groups (spectrum b in Fig. 9). After subsequent impregnation of $HReO_4$ there is a greater reduction in the basic OH group intensity (spectrum c in Fig. 9) as can be expected from the experiments with pure alumina.

Samples 23, 24, and 25 were prepared in solutions buffered with acetic acid and potassium acetate to constant pH (pH 5) to avoid structural changes of the molybdate
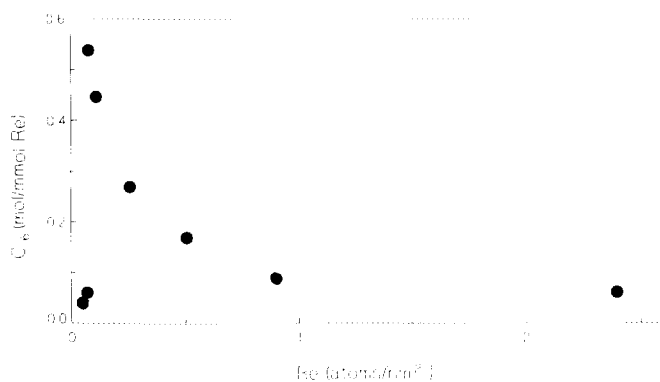

FIG. 8. Effect of rhenium loading on catalyst activity with Re/Al$_2$O$_3$ in ethenolysis of 1,5-cyclooctadiene.
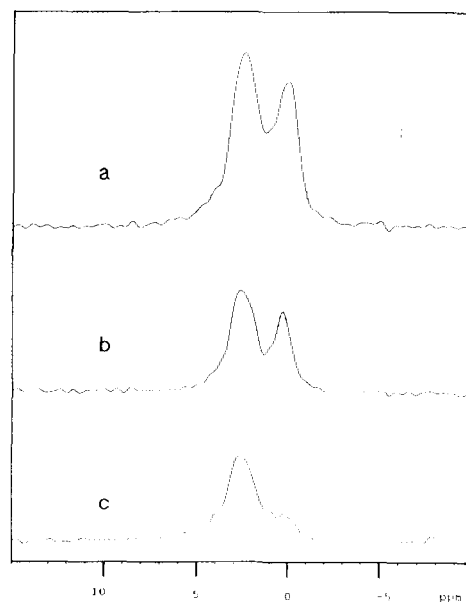

FIG. 9. ^{1}H MAS NMR spectra at 298 K of (a) γ-alumina, (b) Al$_2$O$_3$ + 3.8% Mo (sample 23) and (c) Al$_2$O$_3$ + 4.0% Mo + 1.6% Re (sample 25) calcined at 880 K.

anion. Possible adsorption of the acetate anion on alumina was checked with ^{13}C CP-MAS NMR and was found to be present as evidenced by two peaks in the spectrum at 22 and 182 ppm. However, the peaks disappeared after calcination. The increase of the calculated OH/nm^2 in sample 23 can be at least partially caused by the presence of acetate anions (Table 2). The potassium cation does not attach at this pH (less than 0.01% K in the calcined catalysts). The ΔOH/Mo ratio is less than 2 (Table 2) suggesting that molybdate clusters are present. Raman spectroscopy studies have indicated that MoO$_4^{2-}$, Mo$_7$O$_{24}^{6-}$, and Mo$_8$O$_{26}^{4-}$ can coexist on an alumina surface with their relative abundance depending on molybdenum loading (36).

It is known that adsorption of molybdate anions on alumina increases its Brønsted acidity (19, 37) but this cannot be seen clearly by ^{1}H MAS NMR with moderate Mo loadings. In Table 3 Re/Al$_2$O$_3$ and Re/Al$_2$O$_3$-Mo having Re loadings around 0.27 atom/nm^2 (samples 6 and 25) give C_6 yields of 0.27 mol/mmol and 1.2 mol/mmol, respectively. When only $(NH_4)_2MoO_4$ was impregnated on alumina, no activity was detected (sample 23). Catalysts prepared in nonbuffered solutions of $(NH_4)_2MoO_4$ are also more active than the corresponding Re/Al$_2$O$_3$ catalysts (compare samples 8 and 26 in Table 3).

Al_2O_3 + Cl + Re, Al_2O_3 + F + Re

In Fig. 5 the spectra of the pure alumina are compared with the alumina after adsorption of Cl$^-$ and subsequent
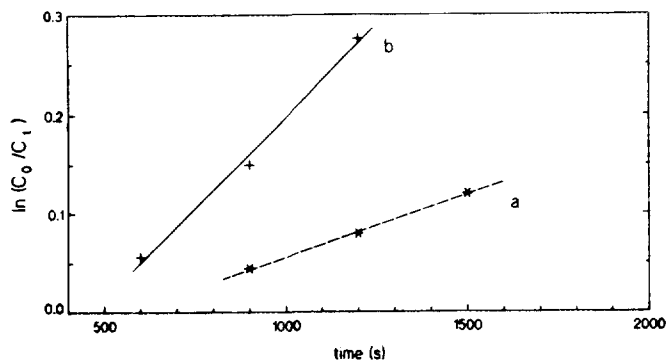
FIG. 10. Observed reaction rates for ethenolysis of 1,5-cycloocta-diene at 298 K with (a) Al_2O_3 + 2.0% Re (sample 7) and (b) Al_2O_3 + 0.80% Cl + 2.0% Re (sample 15). Initial concentration of 1,5-cyclooctadiene is C_0 and the concentration at time t is C_t.

adsorption with Re. The reaction of the Re takes place only with the residual acidic OH groups. The number of OH groups lost per Cl atom is 1, as expected, and again the number of OH groups lost per Re atom is also 1 (Table 2). Fluoride behaves in the same way as chloride, see Fig. 6 and Table 3.

Both Cl^- and F^- increase the specific activity of Re (Table 3). If the consumption of COD is followed after the initiation period and before the building up of a considerable concentration of reaction products, the first order reaction equation can be applied. This is shown in Fig. 10 for two catalysts that both contain 2.0% rhenium (0.34 atoms/nm²). Sample 7 was prepared on pure alumina and sample 15 on alumina containing 1.6% Cl before adsorption of ReO_4^-. The observed rate constants are 1.3×10^{-4} s^{-1} and 3.7×10^{-4} s^{-1}, respectively.

It is known that halogenation of alumina increases the Brønsted acidity of the remaining OH groups (38, 39) and creates more Lewis acidity (40). However, there were no significant side reactions such as double bond isomerization under the mild conditions used in the reaction.

DISCUSSION

The prevailing picture of rhenium oxide coordination on γ-alumina after calcination is based on *in situ* measurements with Raman (9, 41–43) and FT-IR spectroscopy (9, 42) and with XANES (41). There are two almost identical species, one at all loadings and the other at high loadings only. They both possess three terminal Re=O bonds and one bridging Re–O-support bond. The measurements have been carried out on surfaces heated to 673–773 K. An IR study by Sibeijn *et al.* measured the change in OH absorption as a function of rhenium loading on samples heated to about 723 K (10). At loadings around 0.4 atoms/nm² the OH absorbance was larger than with the pure

support but otherwise the OH absorbance decreased quite steadily as Re loading increased. The increase in OH absorbance was explained by formation of Re–OH groups.

The ¹H MAS NMR results of Re/Al₂O₃ catalysts calcined at 880 K show that there are 0.8–1.2 OH groups lost for every Re atom adsorbed at loadings >0.5 atoms/ nm², close to the monodentate bonding model. However, the spectra also show that there appears to be an extra peak at around 5 ppm. If this is an Re–OH group, then the bonding mode is rather different since there will be more Al–OH groups lost per Re atom. Alternatively, it is possible that the presence of Re on the surface results in the formation of very acidic Al–OH groups due to the local electron withdrawing effect. Low loading Re/Al₂O₃ (<0.5 atoms/nm²) seems to behave differently. One equivalent of rhenium can displace up to three equivalents of surface hydroxyls. It is interesting that temperature programmed reduction with hydrogen has indicated that the reduction temperature increases when the concentration of rhenium on γ-alumina surface decreases below 0.5 nm⁻² (42, 44). This suggests an increasing interaction between Re and the support.

It was presumed that the formation of paramagnetic Re could be responsible for the unexpectedly high ΔOH/Re. However, no Re(IV) or Re(VI) could be detected when a sample was examined by ESR spectroscopy at temperatures down to 4 K. We therefore assume that the Re is present as diamagnetic Re (VII) and the NMR measurements are not disturbed by the presence of paramagnetic Re.

Spronk (45) compared the activity of Re/Al₂O₃ + SnEt₄ in propene metathesis when it was calcined at various temperatures between 823 and 1273 K. It was found that the optimum calcination temperature is around 1173 K with a large jump in activity upwards between 923 and 1023 K. We have observed the same kind of jump with Re/Al₂O₃ in COD ethenolysis when the calcination temperature was increased from 830 to 880 K.

Yide *et al.* (46) showed that when Re/Al₂O₃ is treated with propene at 723 K and then flushed with helium at 823 K before reaction, the specific activity in propene metathesis increases when Re loading decreases. Under normal calcination conditions using air the activity increases with increasing Re loading. We observed the former behaviour with Re/Al₂O₃ in COD and ethene metathesis when the catalyst was calcined with air and nitrogen at 880 K and cooled with nitrogen. The initial ratio COD (g)/catalyst (g) was kept constant to ensure that mass transfer between the catalyst surface and the bulk liquid did not vary. Notice that the COD conversion at Re loadings between 0.082 and 2.40 atoms/nm² is almost constant suggesting that the number of active sites is nearly constant in all these catalysts.

Vuurman *et al.* (9) propose two types of rhenium oxide on the γ-alumina surface based on their *in situ* Raman and IR spectroscopy results. They concluded that if there were two main types of OH groups on γ-alumina, the structures could be associated with the reaction of ReO_4^- with these groups. The ^{1}H MAS NMR results indicate that there are indeed two main types of OH groups present on the surface. However, they did not believe that Re is more electron deficient in the high loading catalysts because the Re–O-support bond becomes weaker. Therefore it is not obvious that high loading ctalysts are more active than low loading catalysts.

One can speculate that a strong interaction with the surface is a prerequisite for very active sites because then Re is highly electron deficient. The performance of Re/Al_2O_3 is governed by the amount of a small number of special sites which is constant when the Re loading exceeds a certain value (about 0.08 atoms/nm^2). The profile in Fig. 8 suggests that the real number of these sites is much smaller than 0.08 atoms/nm^2 because the lower loadings are not so active. The state of Re is highly dependent on the heat treatment, as the preceding discussion shows.

When the activity is calculated per metal atom, it is assumed that all the metal atoms take part in the reaction. This is actually very improbable for Re/Al_2O_3 catalysts (47, 48). However, because Re_2O_7 is volatile at calcination temperatures it is usually felt safe to assume that at least the dispersion is good. Our electron back-scattering images of calcined catalysts reveal that even on low-loading catalysts (<0.5% Re) prepared by ion-exchange one can see some rhenium oxide aggregates of the apparent diameter of about 0.1–0.5 μm. Ellison *et al.* (35) have found these structures with XRD, FABMS, and EXAFS. Dry impregnation favours the formation of aggregates because loosely bound material is not removed during the preparation. Therefore comparison of the special activities of the catalysts prepared by dry impregnation and by ion exchange is not straightforward.

Conversion per gram of catalyst can be increased by treating alumina first with an anion capable of reacting with the basic OH groups. Also in this case low Re loadings give the highest special activity. It is interesting that even carboxylic acid anions can produce the same effect (Table 3). This suggests that inductive effects caused by adsorbed anions or bimetallic interactions hardly play any significant role in the activation. Activation with MoO_4^{2-} suggests that the elimination of the most basic of the basic OH groups and possibly Lewis acid sites is the predominating factor because MoO_4^{2-} did not eliminate selectively the basic type of OH groups. This cannot be verified with ^{1}H MAS NMR but it can be followed with FT-IR spectroscopy. We are now studying these catalysts with FT-IR spectroscopy to clarify this area.

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