Catalysis Letters 8 (1991) 201–208

IR STUDIES OF Re_2O_7 METATHESIS CATALYSTS SUPPORTED ON ALUMINA AND PHOSPHATED ALUMINA

M. SIBEIJN, R. SPRONK, J.A.R. van VEEN [a] and J.C. MOL *

Department of Chemical Engineering, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

[a] *Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research B.V.), Badhuisweg 3, 1031 CM Amsterdam, The Netherlands*

Received 20 December 1990; accepted 28 December 1990

FTIR data from Re_2O_7/γ-Al_2O_3 metathesis catalysts indicate that a low Re contents ReO_4^- ions have predominantly reacted with basic surface OH groups, while at higher Re_2O_7 loadings they have also reacted with neutral and more acidic OH groups.

On phosphated γ-Al_2O_3 the phosphate has reacted with the more acidic OH groups on the γ-Al_2O_3; in catalysts based on this support, the ReO_4^- ions have also reacted with the phosphorus-bonded OH groups already at low Re_2O_7 loadings, resulting in more active catalysts.

Keywords: Metathesis, infrared, surface hydroxyl groups, rhenium oxide, alumina, phosphated alumina

1. Introduction

Re_2O_7/γ-Al_2O_3 is one of the most active and widely used heterogeneous catalysts for the metathesis of alkenes. With this catalyst the reaction may be carried out at 20–100 °C with the substrate alkene either in the gas phase or in the liquid phase. The metathesis of propene:

$$2CH_2{=}CH\text{-}CH_3 \leftrightharpoons CH_2{=}CH_2 + CH_3\text{-}CH{=}CH\text{-}CH_3$$

has frequently been used as a model reaction to study the activity of this catalyst. The turnover frequency, i.e. the activity per Re atom, appears to be very low at low Re_2O_7 loading and increases sharply above a Re_2O_7 loading of approx. 6 wt% [1].

Recently we have been able to come up with a theory that can explain this behaviour [2,3]. This theory is based on a reaction between ReO_4^- ions and the surface OH groups of the support during the preparation of the catalyst [4]. On γ-Al_2O_3 five types of OH groups are present, which have different calculated

---

* Corresponding author.

charges, varying from -0.5 to $+0.5$ [5]. Usually, a Re_2O_7/Al_2O_3 metathesis catalyst is prepared by impregnation of the alumina support with an aqueous ammonium perrhenate solution, followed by drying in air. After O_2 calcination at 823 K, rhenium oxide forms a monolayer, existing of Al-bounded ReO_4 groups formed after the reaction of ReO_4^- ions with the surface OH groups [1]. These surface ReO_4 groups will have electronic properties which depend on the type of the hydroxyl group they have replaced. We deduced that the ReO_4^- ions first mainly react with basic (negatively charged) hydroxyl groups, resulting in inactive metathesis sites, because the Re centre is too electron-rich to allow, for instance, the complexation of the carbon-carbon double bond of an alkene during metathesis [2,3]. At higher loadings relatively more acidic (positively charged) OH groups have reacted with the ReO_4^- ions, which does result in active sites, because an electron-deficient Re centre is formed, which will easily accept the complexation of a double bond.

In the present study an attempt is made to verify this theory by means of infrared spectroscopy, which allows one to study the various hydroxyl groups present on supported catalysts.

An interesting way to increase the catalytic activity of γ-Al_2O_3-supported Re_2O_7 catalysts is treating the support with phosphate prior to impregnation with NH_4ReO_4 [6]. This empirical finding has never been rationalized in terms of surface composition. Recently it was demonstrated that modification of the γ-Al_2O_3 surface with phosphate results in a more acidic surface [7]. Therefore, we compared the activity of a Re_2O_7 catalyst supported on phosphated γ-Al_2O_3 with the corresponding γ-Al_2O_3-supported catalyst in propene metathesis, and subsequently also studied the surface of these phosphated catalysts by means of infrared spectroscopy.

In the study of catalytic reactions, like alkene metathesis, knowledge about the active site (or its precursor) and how they can be created is essential. Therefore it is important to have spectroscopic evidence for our proposed theory, which may help in the development of new (metathesis) catalysts.

2. Experimental

CATALYST PREPARATION

The support γ-Al_2O_3 type CK-300 (BET-surface area = 208 m^2/g; $V_p = 0.51$ cm^3/g) was obtained from AKZO Chemicals b.v. It was ground and sieved, and the 180–250 μm-fraction was used. The phosphated Al_2O_3 was obtained by treating a sieved fraction (180–250 μm) of the γ-Al_2O_3 with $(NH_4)_2HPO_4$ as described in the US Patent 3,974,233 example 3 [6]. First the γ-Al_2O_3 was calcined in an air stream at 823 K for 18 h and subsequently cooled to room temperature. 100 g of this support was digested with 400 mL of an aqueous solution containing 10 g of $(NH_4)_2HPO_4$. The suspension was stirred at 353 K for 6 h. The excess liquid was filtered off and the treated support was subsequently dried overnight at 383 K, after which it was calcined at 873 K for 18 h. The calculated P content of this support is 2.2 wt%, the BET-surface area = 160 m^2/g and $V_p = 0.38$ cm^3/g.

The Re_2O_7 catalysts were prepared by pore-volume impregnation of the supports with calculated amounts of an aqueous solution of ammonium perrhenate (Johnson Matthey Chemicals Ltd., JMC 836 Specpure), followed by overnight drying 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.

INFRARED MEASUREMENTS

Before the IR spectra were recorded the catalysts were calcined in oxygen (50 ml/min) at 823 K for 2 h (heating rate 10 K/min), and subsequently exposed to air. IR spectra were recorded on a Digilab FTS 15E, using self-supporting disks of a 20 mg sample (approx. 8 $mg.cm^{-2}$). Before a spectrum was recorded, the sample was evacuated at $T \geqslant 723$ K, in order to obtain well resolved spectra.

ACTIVITY MEASUREMENTS

The activity of the catalysts in the metathesis of propene was measured in a conventional microcatalytic fixed-bed flow reactor. Details about the reactor set-up are given elsewhere [2]. The catalyst was activated in-situ in oxygen (50 ml/min) at 823 K for 2 h (heating rate 10 K/min), followed by a nitrogen purge at the same temperature for 15 min.

Standard reaction conditions were a contact time (W/F) of 11.55 kg(cat).s/mol, a pressure of 1.5 bar and a reaction temperature of 353 K.

3. Results and discussion

1. ALUMINA

In principle five different types of OH groups can be detected on γ-Al_2O_3; two types with a basic character, one neutral type and two types with an acidic character [5]. Roughly speaking, the OH stretch region of the IR spectrum consists of three band systems: at 3775 cm^{-1} (basic OH groups), at 3730 cm^{-1} (neutral OH groups) and at 3690 cm^{-1} (acidic OH groups) [8].

Fig. 1 shows the IR spectra of Re_2O_7/γ-Al_2O_3 catalysts with Re_2O_7 loadings of 0, 3, 6, 12 and 18 wt%, respectively. The three previously mentioned band systems are observed in the OH-stretching region of 3200 cm^{-1} to 4000 cm^{-1}. After a slight increase, they all decrease with increasing rhenium loading, suggesting that the surface OH groups have reacted with ReO_4^- ions. In fig. 2a the absorbances (peak heights) of these three types of OH groups are plotted against the Re_2O_7 loading of the catalysts. All data points were measured in duplicate, showing

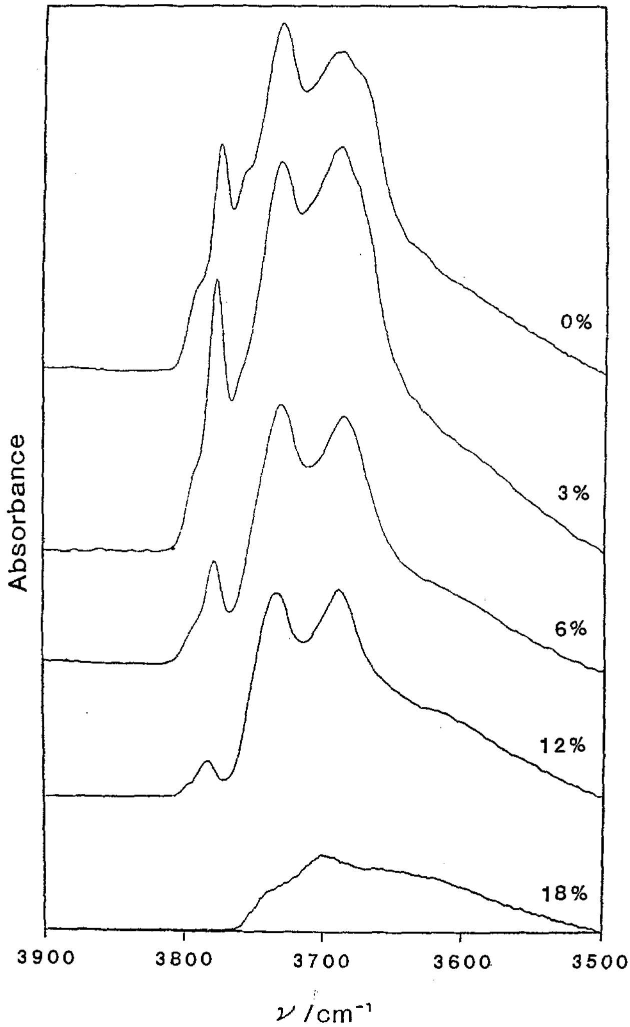

Fig. 1. FTIR spectra in the OH stretching region of $Re_2O_7/\gamma\text{-}Al_2O_3$ catalysts with varying Re_2O_7 loadings.

excellent reproducibility. Average values, corrected for both sample weight and rhenium loading, are used in the figure.

From fig. 2a it can be concluded that at very low Re_2O_7 loadings the absorbances of all types of OH groups increase slightly. This indicates that the ReO_4^- ions probably do not react with OH groups in the first instance, but are adsorbed on coordinatively unsaturated (cus) Al^{3+} surface sites (Lewis acid sites) [8]. This adsorption of ReO_4^- ions on cus Al^{3+} sites might result in the formation of new OH groups attached to these adsorbed Re centres, which could explain the slight increase in absorbance at low Re loadings. When the cus Al^{3+} sites are saturated, no new Re-OH groups are formed and the ReO_4^- ions react with the

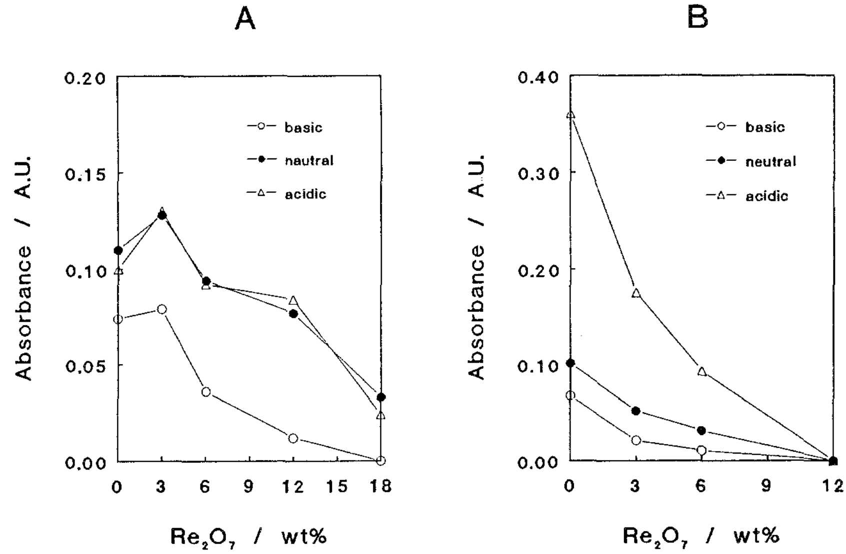

Fig. 2. The absorbances of the three different types of OH groups as a function of the Re_2O_7 loading of the $Re_2O_7/\gamma\text{-}Al_2O_3$ catalysts (A) and the $Re_2O_7/Al_2O_3.AlPO_4$ catalysts (B) (corrected for sample weight and rhenium loading).

surface hydroxyls. At loadings of about 3–12 wt% Re_2O_7 it appears that the ReO_4^- ions predominantly react with the basic OH groups (3775 cm^{-1}) and to a lesser extent with the non-basic OH groups. At higher Re_2O_7 loadings relatively more ReO_4^- ions react with the neutral and acidic OH groups. At a 18 wt% Re_2O_7 loading nearly all surface hydroxyls have reacted with ReO_4^- ions; the remaining absorption in the region of acidic and neutral OH groups can then principally be ascribed to the OH groups bonded to Re adsorbed on the cus Al^{3+} sites.

There is a strong correlation between the increase in turnover frequency in propene metathesis as a function of the Re_2O_7 loading [1] and the decrease in the number of acidic surface OH groups. We therefore conclude that the reaction of a ReO_4^- ion with an acidic OH group is a prerequisite for the formation of an active metathesis site. Although two types of acidic OH groups can be recognized in the spectrum of the bare support, in the spectra of the Re-containing catalysts this information is lost. Therefore it could well be that only the ReO_4 groups that have replaced the most acidic OH groups will become really active in metathesis.

2. PHOSPHATED ALUMINA

The activity of a 6 wt% $Re_2O_7/Al_2O_3.AlPO_4$ catalyst in propene metathesis was measured and compared with the activity of the corresponding $\gamma\text{-}Al_2O_3$-supported catalyst (fig. 3). It appears that under our experimental conditions the phosphated catalyst is roughly twice and active as the $\gamma\text{-}Al_2O_3$-supported one.

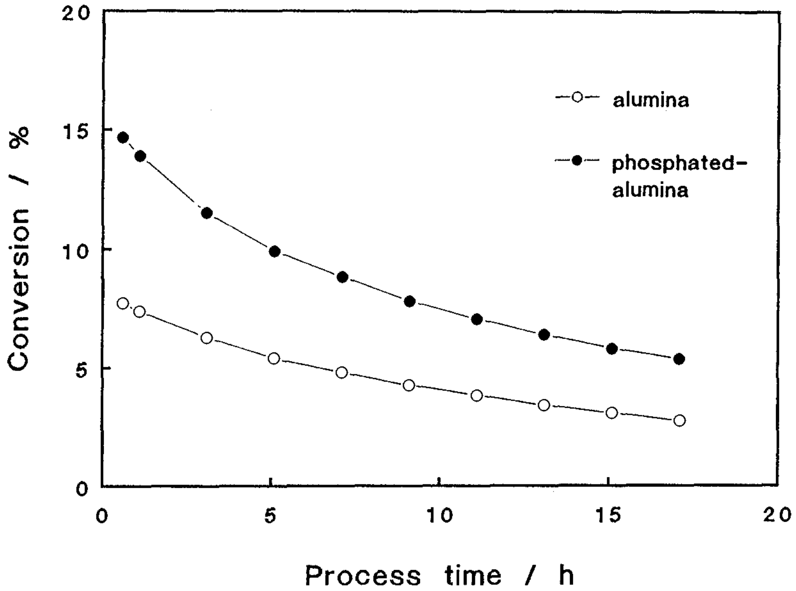

Fig. 3. The activity of 6 wt% $Re_2O_7/\gamma\text{-}Al_2O_3$ and 6 wt% $Re_2O_7/Al_2O_3.AlPO_4$ in the metathesis of propene at 353 K as a function of the process time. $W/F = 11.55$ kg(cat).s/mol; $P = 1.5$ bar.

Corresponding results have been obtained in the metathesis of functionalized alkenes, such as methyl oleate [9].

The IR spectra of $\gamma\text{-}Al_2O_3$ and phosphated $\gamma\text{-}Al_2O_3$ are shown in fig. 1 and fig. 4, respectively, whereas the absorbances of all types of OH groups on these supports are given in figs. 2a and 2b, respectively. The most remarkable difference is the appearance of an intense new band at 3680 cm^{-1} in the spectrum of the phosphated alumina, belonging to acidic ≡P-OH groups [10]. The absorption band due to the acidic OH groups bonded to Al cannot be observed, because of this overlapping new absorption band. The intensities of the absorption bands due to the neutral and basic OH groups have decreased slightly, which can be attributed to the destruction of the Al_2O_3-surface by formation of $AlPO_4$ formed upon reaction of $\gamma\text{-}Al_2O_3$ with phosphate. It is therefore most likely that the PO_4^- ions react with the acidic OH groups on Al_2O_3 to form ≡P-OH [8], although it is not possible to say whether all acidic OH groups on $\gamma\text{-}Al_2O_3$ have reacted with phosphate.

Fig. 4 shows the IR spectra of $Re_2O_7/Al_2O_3.AlPO_4$ catalysts with Re_2O_7 loadings of 0, 3, 6 and 12 wt%, respectively. In fig. 2b the absorbances of the three types of OH groups in these catalysts are plotted as a function of the Re_2O_7 loading, corrected for sample weight and rhenium loading. It becomes clear that the relative decrease of all OH groups is equal; at 12 wt% Re_2O_7 all peaks have disappeared. Apparently ReO_4^- ions have no preference for any of the OH groups. As the acidic OH groups bonded to phosphorus react with the ReO_4^- ions

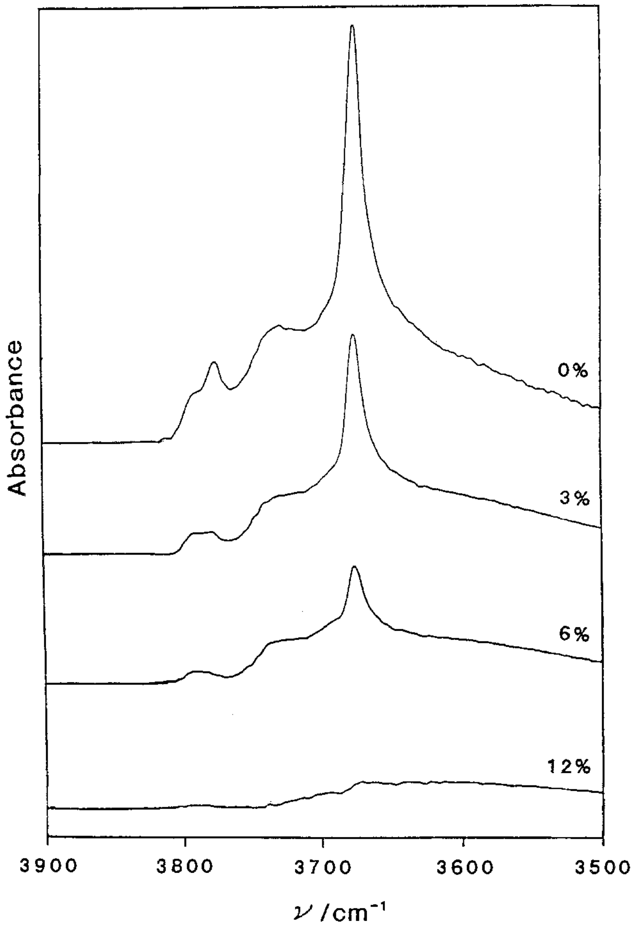

Fig. 4. FTIR spectra in the OH stretching region of the $Re_2O_7/Al_2O_3.AlPO_4$ with varying Re_2O_7 loadings.

already at low Re loadings, the activity of a low-loaded catalyst will be higher than that of the corresponding γ-Al_2O_3-supported catalyst.

4. Conclusions

FTIR-measurements support the idea that the active metathesis site of Al_2O_3-supported Re_2O_7 catalysts is an electron-deficient Re centre. These sites are formed when ReO_4^- ions react with the more acidic OH groups to form Al-bonded ReO_4 groups on the catalyst surface. The sharp increase in activity of γ-Al_2O_3-supported catalysts for propene metathesis, above a 6 wt% Re_2O_7 loading, is due to the relative increase in the number of electron-deficient Re centres at higher loadings. Almost no activity is obtained at low Re_2O_7 loadings, as the

ReO_4^- ions have then predominantly reacted with the cus Al^{3+} sites and subsequently with the more basic OH groups.

The modification of Al_2O_3 with $(NH_4)_2HPO_4$ results in a more active Re_2O_7 catalyst, as the more acidic OH groups on γ-Al_2O_3 have reacted with the phosphate to form acidic ≡P-OH groups. In the catalysts based on this support, the ReO_4^- ions have also reacted with the phosphorus-bonded OH groups, already at low Re loadings. This accounts for the fact that Re_2O_7 catalysts supported on phosphated Al_2O_3 are more active than the corresponding catalysts supported on γ-Al_2O_3.

References

[1] J.A. Moulijn and J.C. Mol, J. Mol. Catal. 46 (1988) 1.
[2] R. Spronk, A. Andreini and J.C. Mol, Proc. 8th Int. Symp. on Metathesis, Bayreuth, 1989, J. Mol. Catal., in press.
[3] M. Sibeijn and J.C. Mol, Appl. Catal., in press.
[4] A.A. Olsthoorn and C. Boelhouwer, J. Catal. 44 (1976) 197.
[5] H. Knözinger and P. Ratnasamy, Catal. Rev.-Sci. Eng. 17 (1978) 31.
[6] M.J. Lawrenson (to B.P.), US Patent 3,974,233 (1976); GB Patent 2.131,429 (1984).
[7] A. Stanislaus, M. Absi-Halabi and K. Al-Dolama, Appl. Catal. 39 (1988) 239.
[8] J.A.R. Van Veen, G. Jonkers and W.H. Hesselink, J. Chem. Soc., Faraday Trans. 1, 85 (1989) 389.
[9] J.C. Mol, Proc. 8th Int. Symp. on Metathesis, Bayreuth, 1989, J. Mol. Catal., in press
[10] J.A.R. Van Veen, P.A.J.M. Hendriks, R.R. Andréa, E.J.G.M. Romers and A.E. Wilson, J. Phys. Chem. 94 (1990) 5282.