JOURNAL OF CATALYSIS **174,** 119–129 (1998)
ARTICLE NO. CA981956

The Influence of Pretreatment on the Metal Function of a Commercial Pt–Re/Al_2O_3 Catalyst

Rune Prestvik,* Kjell Moljord,†,[1] Knut Grande,‡ and Anders Holmen*,[2]

*Department of Industrial Chemistry, Norwegian University of Science and Technology (NTNU), N-7034 Trondheim, Norway; †SINTEF Applied Chemistry, N-7034 Trondheim, Norway; and ‡Statoil Research Centre, Postuttak, N-7005 Trondheim, Norway

Received April 21, 1997; revised October 3, 1997; accepted October 3, 1997

The metal function of a commercial 0.3–0.3 wt% Pt–Re/Al_2O_3 catalyst was characterized by temperature-programmed reduction, by H_2 and O_2 chemisorption, and by using methylcyclohexane dehydrogenation and *n*-heptane conversion as model reactions. Emphasis was put on investigating the influence of the drying conditions prior to reduction. The degree of hydration of the catalyst, as set by the drying temperature, strongly modifies the reducibility of rhenium and the extent of alloy formation in the reduced catalyst. Alloy formation affects the chemisorption characteristics and the hydrogenolysis activity of the catalyst. Platinum dispersion was not affected by air pretreatment at temperatures up to 680°C, while in nitrogen, platinum oxide decomposition and sintering were observed from 400°C and higher. The presence of water vapor during H_2 reduction was found to promote Pt sintering.

1. INTRODUCTION

Catalytic reforming of naphtha is performed using a bifunctional catalyst containing both a metallic and an acidic function. The metal is Pt usually in combination with another component such as Re, Sn, Ir, or Ge. The acidic function is normally provided by a high surface area, chlorine promoted γ-Al_2O_3 support. It is well demonstrated that the addition of rhenium to Pt/Al_2O_3 results in a catalyst with greater stability (1). However, the exact role of rhenium in Pt–Re catalysts has been a matter of controversy. It has been proposed that rhenium acts independently and is able to convert coke precursors into harmless products (2) and that rhenium anchors platinum to the alumina, stabilizing the platinum dispersion (3). A common view for explaining the properties of Pt–Re/Al_2O_3 is that of Pt–Re alloy formation (4) and the interaction of such an alloy with sulfur (5–8). The improved properties of Pt–Re/Al_2O_3 are observed only in the presence of a limited amount of adsorbed sulfur. The higher stability of rhenium-containing catalysts has been shown to result from the nature rather than the amount of carbon deposited on the catalyst surface (9). It has been suggested that sulfur adsorbs primarily on rhenium which, in the case of mixed Pt–Re ensembles, divides the Pt–Re surface effectively into small platinum entities. These small platinum entities are too small for the formation of harmful graphitic coke as well as for unwanted and demanding hydrogenolysis reactions (6–8).

It has been shown (10–13) using temperature-programmed reduction (TPR) that the degree of catalyst hydration, as set by the drying temperature prior to reduction, strongly affects the reducibility of rhenium. On a hydrated catalyst, rhenium reduction is catalyzed by Pt, resulting in simultaneous reduction of platinum and rhenium at a low temperature (∼300°C). Upon dehydration, rhenium oxide is reduced at progressively higher temperatures. After drying at 500°C, rhenium reduction occurs only at an elevated temperature (∼600°C) as in the case of monometallic Re/Al_2O_3. Two main theories have been proposed to explain these observations. One theory is that the degree of hydration influences the mobility of rhenium oxide (10, 11). It is suggested that after drying at low temperature, rhenium oxide is mobile and can migrate over the hydrated catalyst to reduced Pt, where atomic hydrogen is supplied for its reduction. Upon dehydration, the mobility of rhenium oxide is decreased, resulting in separate reduction of Re at higher temperatures. The other theory (12) is that the degree of hydration influences hydrogen spillover. Thus, on a hydrated support, hydrogen may spill over from reduced platinum to rhenium oxide which is then reduced. Catalyst dehydration lowers the rate of spillover, thus increasing the reduction temperature of rhenium. There is a distinct difference between the two reduction mechanisms; the former suggests that rhenium may be alloyed with platinum, while the latter suggests that Pt and Re exist as separate entities after reduction. Supportive results for alloy formation has been provided by Augustine and Sachtler (14), using cyclopentane hydrogenolysis as a probe reaction for alloy formation. It was found that the

---

[1] Present address: Statoil Research Centre, Postuttak, N-7005 Trondheim, Norway.

[2] To whom correspondence should be addressed. Fax: +4773595047. E-mail: holmen@chembio.ntnu.no.

rate of hydrogenolysis was much higher when the catalyst had been reduced directly (without drying) than when the catalyst had been dried in Ar at 500°C prior to reduction. Little attention has been paid to the influence of the drying atmosphere on catalyst reducibility and to alloy formation. The cited literature has to a large extent utilized He or Ar as drying atmospheres and some results (13) indicate that platinum oxide is subjected to decomposition at temperatures below 500°C. In addition, somewhat different TPR profiles have been reported (15) using air as the drying atmosphere.

The purpose of the present work is to further elaborate on the effects of the drying temperature and atmosphere (inert or oxidizing) on the metal function of a Pt–Re/Al_2O_3 catalyst. TPR is applied to examine the reducibility of the metal components. The drying temperature determines the amount of water on the catalyst prior to reduction. Since the presence of water during reduction is known to promote platinum sintering (16), it is of interest also to measure the Pt dispersion as a function of the drying conditions. The addition of water to the reducing gas is investigated. Methylcyclohexane dehydrogenation, a structure-insensitive reaction (17), not being influenced by the presence of rhenium, is chosen as a model reaction for the Pt dispersion. Chemisorption studies (18, 19) have shown that the drying temperature strongly influences the chemisorption properties of Pt–Re/Al_2O_3 catalysts due to alteration of the metal crystallite composition. Chemisorption measurements are therefore conducted to provide information of the extent of alloy formation rather than the metal dispersion. At last, *n*-heptane conversion is performed to further investigate the effect of alloy formation on product selectivity.

2. EXPERIMENTAL

2.1. Catalysts

The catalysts used were commercial 0.3 wt% Pt/Al_2O_3 (CK 303; EUROPT-3), 0.3–0.3 wt% Pt–Re/Al_2O_3 (CK 433; EUROPT-4), and γ-Al_2O_3 (CK 300), manufactured by Akzo. The chloride loadings of the Pt and Pt–Re catalysts were 1.0 and 0.95 wt%, respectively. The detailed data on these catalysts are given elsewhere (20). The commercial extrudates were crushed and sieved and the particles with the size of 0.25 to 0.60 mm were used. A 0.3 wt% Re/Al_2O_3 catalyst was prepared in this laboratory by incipient wetness impregnation of the γ-Al_2O_3 support (CK 300) with rhenium heptoxide in aqueous solution. The catalyst was calcined in air at 500°C (4 h).

2.2. Temperature-Programmed Reduction and Pulse Chemisorption

A standard Rogers–Amenomiya–Robertson arrangement (21) was used to perform TPR and pulse chemisorption experiments. The apparatus is described elsewhere (22). All the gases utilized were purified by molsieves and O_2 traps.

TPR was conducted using catalyst samples of about 1 g. The samples were heated slowly, 0.8°C/min and dried at a chosen temperature, T_D, for 4 h in flowing air or N_2 (30 ml/min), before cooling to ambient conditions. The samples were then exposed to a 7% H_2 in Ar mixture (30 ml/min) and heated by 10°C/min to 550°C and kept at this temperature 30 min or longer. The H_2 consumption was monitored by a thermal conductivity detector (TCD).

Pulse chemisorption measurements were performed in the same apparatus. Catalyst samples of 1–2 g were dried in either air or N_2 (30 ml/min) at a chosen temperature, T_D, for 4 h. For $T_D < 400°C$, the catalyst sample was flushed in Ar for 5 min and then exposed to H_2 (30 ml/min) and heated at a rate of 2.4°C/min to 480°C. For $T_D \geq 400°C$, the sample was cooled to 400°C, flushed in Ar for 5 min, exposed to H_2 and heated at 0.8°C/min to 480°C. After 1 h of reduction at 480°C the sample was cooled to 400°C, flushed in Ar for 1 h, and cooled to 20°C. The chemisorption procedure involved injecting pulses of either H_2 or O_2 into the Ar stream. From the number of pulses chemisorbed by the sample, the amount of gas chemisorbed by the catalyst was calculated.

2.3. Activity Measurements

Methylcyclohexane dehydrogenation and *n*-heptane conversion measurements were performed in a stainless-steel microreactor described in detail elsewhere (22). Drying and reduction was performed at 1 bar as described for the chemisorption measurements. Conversion data were obtained by on line GC analysis of the reactor effluent. A HP 5890 gas chromatograph equipped with a flame ionization detector (FID) was used. The C_1 to C_{10} hydrocarbons were separated on a 50-m GS alumina column (J&W Scientific). Methylcyclohexane (MCH) dehydrogenation was performed using samples of 0.1 g catalyst. The reaction was carried out at 300°C, 1.1 bar, WHSV = 25 h^{-1}, and a H_2/MCH ratio of 40. Experiments investigating the effect of water vapor in the H_2 gas during reduction were performed by saturating the H_2 gas over a bed of ice particles at −20.2 or −2.2°C, giving 0.1 and 0.5 mol% H_2O in H_2, respectively (23).

n-Heptane conversion was performed using catalyst samples of 1 g, 505°C, 16 bar, WHSV = 10 h^{-1}, and a ratio between H_2 and *n*-heptane of 10. To avoid a possible temperature increase during start-up, the initial reactor temperature was set to 400°C during introduction of *n*-heptane.

2.4. Transmission Electron Microscopy

Transmission electron microscopy (TEM) was performed using a Philips CM 30 microscope operated at 150–300 kV. The samples were pretreated and reduced outside the microscope (using the TPR/chemisorption apparatus) and stored in bottles until TEM analysis was performed.

2.5. *Thermogravimetric Analysis*

Thermogravimetric analysis (TGA) was performed using a Perkin Elmer TGA 7 thermogravimetric analyzer. Forty milligrams of catalyst samples was heated in either air + N_2 (30 + 20 ml/min) or N_2 (20 ml/min), from ambient temperature up to 680°C. The temperature was maintained at 680°C for 4 h.

2.6. *Chlorine Analysis*

Chlorine analysis was done by Escha dissolution of the sample and silver nitrate titration using chromate as indicator (Mohr method). This analysis gives the total amount of chlorine in the sample.

3. RESULTS

3.1. *Temperature-Programmed Reduction*

Figure 1 shows the reduction profiles of 0.3 wt% Pt/Al_2O_3 and 0.3 wt% Re/Al_2O_3 dried in air at 150 and 240°C, respectively. Pt reduction is seen as two peaks; a large peak appearing at 250–300°C and a smaller peak at a temperature of around 400°C. The hydrogen consumption of 31.3 μmol/g is close to the theoretical (30.3 μmol/g) for complete reduction of Pt^{+4} to Pt^0. The reduction of Re starts at about 500°C and ends up in a large peak at around 600°C. The hydrogen consumption corresponds to only 55% reduction of rhenium when assuming that Re^{+7} is the oxidation state prior to reduction.

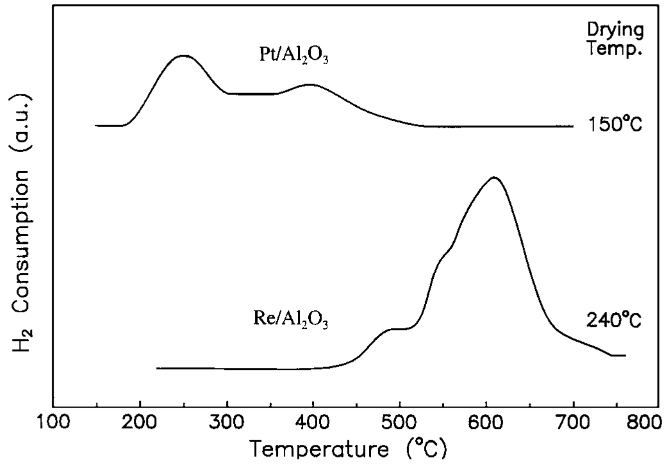

FIG. 1. TPR profiles of Pt/Al_2O_3 after drying in air at 150°C and of Re/Al_2O_3 after drying in air at 240°C

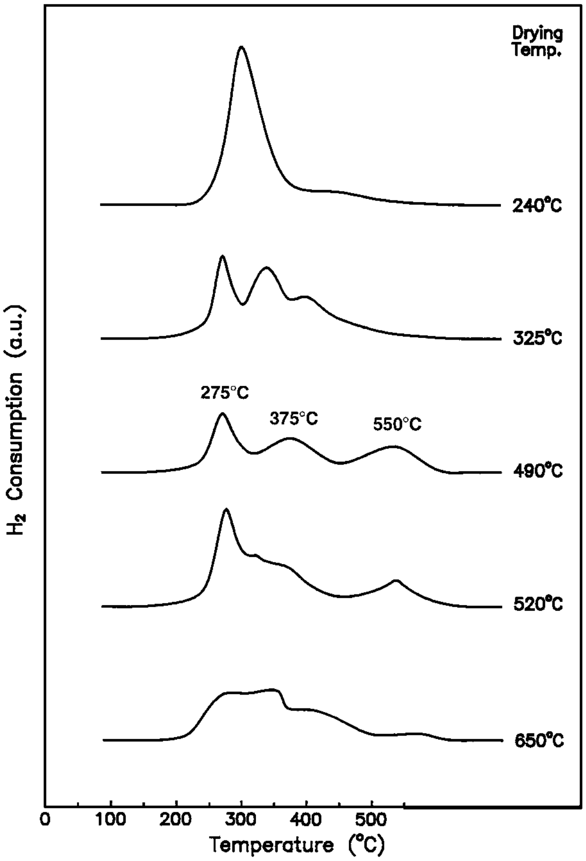

FIG. 2. TPR profiles of Pt–Re/Al_2O_3 obtained after drying in air at different temperatures.

Figures 2 and 3 show the reduction profiles of the 0.3–0.3 wt% Pt–Re/Al_2O_3 catalyst after drying in air and N_2, respectively. The drying temperature was varied from 240°C up to 680°C. The temperature during reduction was programmed up to 550°C and kept at this temperature until the rate of reduction was zero. When the catalyst was dried in air at 240°C (Fig. 2) the reduction profile shows only one TPR peak at 300°C. The H_2 consumption corresponds to a complete reduction of both Pt and Re; thus it is evident that the presence of Pt significantly lowers the temperature of Re reduction since monometallic Re was reduced at 600°C. Increasing the drying temperature results in a deconvolution into three TPR peaks. One peak appears at 275°C, characteristic of monometallic Pt, whereas the other two peaks gradually appear at higher temperatures. After drying at 490°C, the area of the peak at 275°C corresponds to the reduction of all the Pt in the sample. The peaks at 370 and 550°C are therefore probably Re and the first peak can result from the catalytic reduction of Re by Pt while the latter is probably monometallic Re reduction. An increase in the drying temperature up to about 500°C results in increasing reduction temperatures for Re, and a considerable part of Re is reduced at a temperature which is typical for monometallic Re. However, as shown in Fig. 2, increasing the drying temperature to 520 and 650°C reverses this tendency and a lowering of the Re reduction temperature is

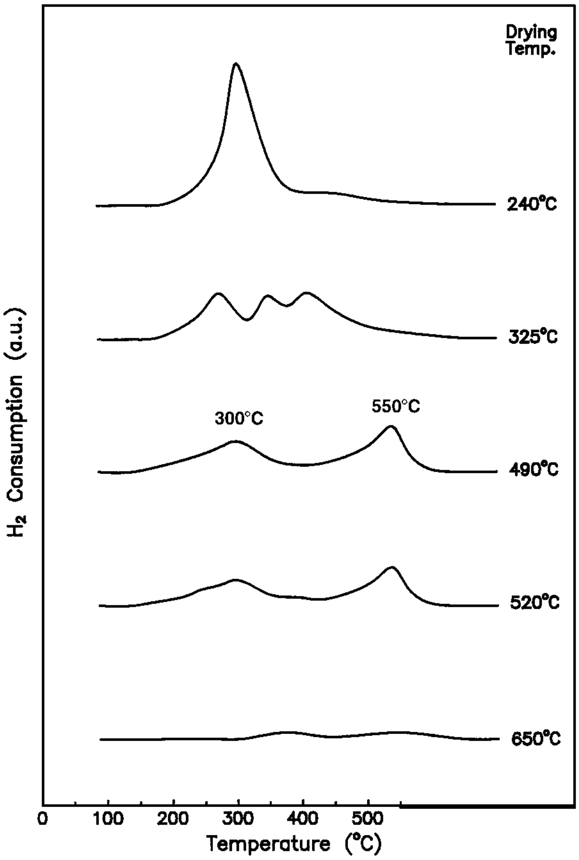

FIG. 3. TPR profiles of Pt–Re/Al_2O_3 obtained after drying in N_2 at different temperatures.

observed. The reduction of Re is probably again catalyzed by Pt. Figure 3 shows TPR profiles after drying in N_2 atmosphere. Drying at 240°C results in one TPR peak at 300°C as was found when air was used during the drying. Increasing the drying temperature to 325°C again results in a deconvolution into three TPR peaks, but after 490°C in N_2 only two peaks appear, characteristic of monometallic Pt and Re. No Re reduction at lower temperature is observed. Increasing the drying temperature to 520 and 680°C does not change the positions of these two peaks, but both the Pt and the Re peaks become smaller. After drying at 680°C in N_2, the H_2 consumption is very low (Fig. 3).

In Fig. 4 the total H_2 consumption during TPR measurements is shown. When drying in air at low temperature, the hydrogen consumption corresponds to the complete reduction of Pt^{+4} to Pt^0 and Re^{+7} to Re^0. After drying at 490°C in air Re was reduced at higher temperatures and the hydrogen consumption was lower, indicating that part of Re is not reduced to the zero valent state. By increasing the drying temperature to 680°C, the H_2 consumption again increases slightly as a result of increased degree of Re reduction. When drying in N_2 at 240°C, the hydrogen consumption is similar to what was found when drying in air. However, a further increase in the drying temperature results in a decrease in H_2 consumption, more pronounced than when air was used. When the drying temperature exceeds 500°C, hydrogen consumption drops rapidly toward zero.

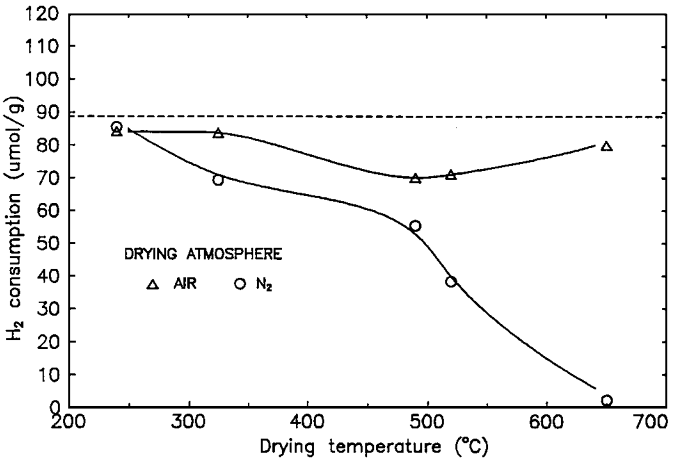

FIG. 4. Effect of drying temperature and atmosphere on H_2 consumption during TPR of Pt–Re/Al_2O_3. The dashed line indicates the theoretical H_2 consumption for complete reduction ($Pt^{+4} \rightarrow Pt^0$ and $Re^{+7} \rightarrow Re^0$).

Figure 5 shows the weight loss of Pt–Re/Al_2O_3 as a function of time as the temperature is increased (0.8°C/min) to 680°C. A marked decrease in weight is observed up to about 150°C, indicating that the catalyst contains 4 to 5 wt% loosely bound water. When the temperature is further increased, the catalyst continues to lose weight until 680°C and by then the total weight loss was 6.7%.

Analysis of total chlorine content of the catalyst indicates that drying at temperatures up to 500°C does not result in any chlorine loss. After drying at 680°C in air, the chlorine content was reduced from 0.97 wt% (fresh catalyst) to 0.88 wt%. After drying in N_2 at the same temperature the total amount of chlorine was 0.84 wt%.

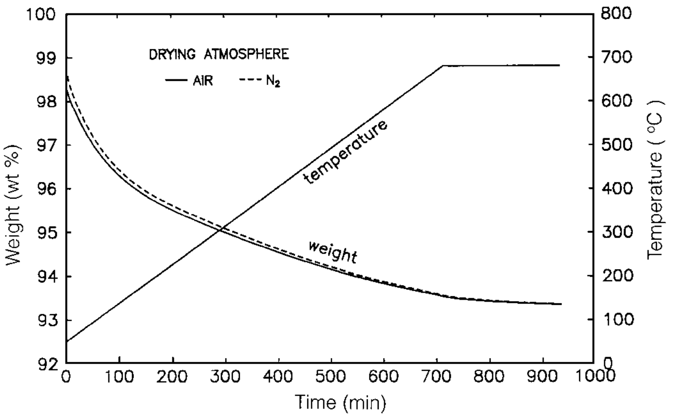

FIG. 5. Effect of drying temperature on the weight reduction of Pt–Re/Al_2O_3 during TGA.

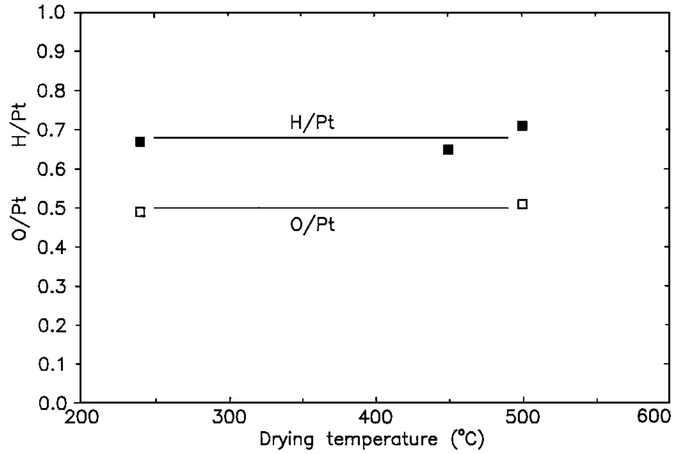

FIG. 6. Effect of drying temperature on hydrogen and oxygen chemisorption for Pt/Al_2O_3 dried in air.

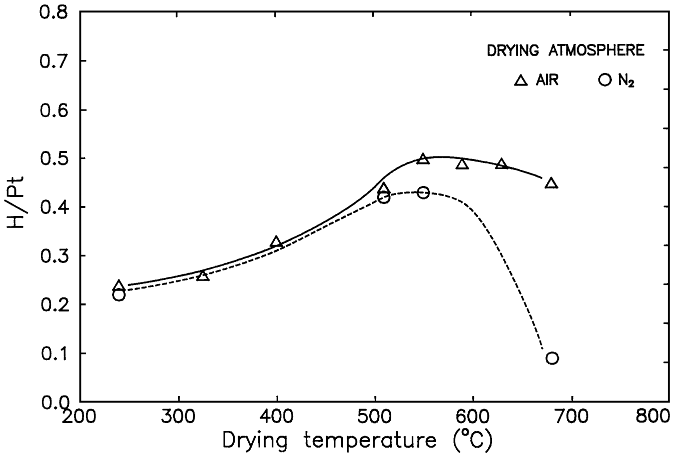

FIG. 8. Effect of drying temperature and atmosphere on hydrogen chemisorption for Pt–Re/Al_2O_3.

3.2. H_2 and O_2 Chemisorption

Figure 6 shows the results of O_2 and H_2 chemisorption on the monometallic Pt/Al_2O_3 catalyst after drying in air at different temperatures. The figure shows that the measured chemisorption is independent of drying temperature, indicating that the Pt dispersion is unaffected by the drying temperature. O_2 chemisorption after drying at 500°C in N_2 atmosphere shows an O/Pt value of 0.39, suggesting sintering of Pt oxide at high temperature when oxygen is not present. The value after drying in air at 500°C was 0.51.

O_2 chemisorption of the Pt–Re/Al_2O_3 catalyst as a function of the drying temperature and atmosphere is given in Fig. 7. O_2 chemisorbs on both Pt and Re atoms (18). The measured O/(Pt + Re) value therefore represents the total dispersion, i.e., the fraction of Pt and Re atoms capable of chemisorbing oxygen. After pretreatment in air at 240°C, the total dispersion is 0.66. Increasing the temperature to 550°C results in decreasing O/(Pt + Re) values. However, a further increase of the drying temperature in air shows that the total dispersion again increases. This pattern corresponds well with the TPR data, which shows lower H_2 consumption after drying at 500°C (Fig. 4). These results indicate that the oxygen chemisorption is probably related to the degree of Re reduction. Drying in N_2 results in lower O/(Pt + Re) values when compared to air drying, suggesting Pt sintering at the higher temperatures.

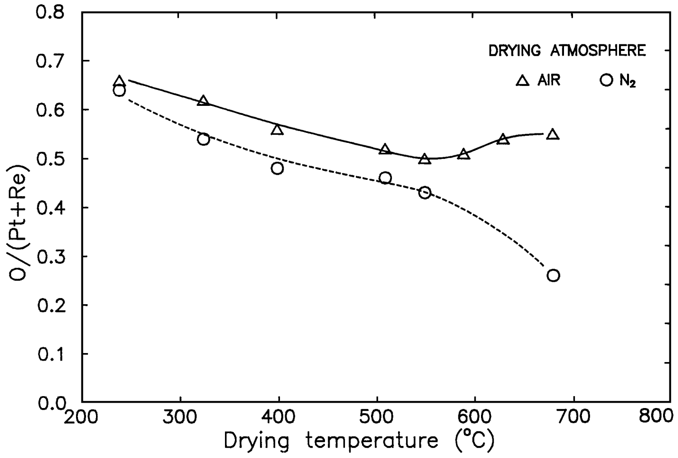

FIG. 7. Effect of drying temperature and atmosphere on oxygen chemisorption for Pt–Re/Al_2O_3.

Figure 8 shows the results of H_2 chemisorption on Pt–Re/Al_2O_3. Drying in air at 240°C gives a H/Pt ratio of only 0.24. Increasing the drying temperature prior to reduction results in increased hydrogen chemisorption. After treatment at 550°C the H/Pt value is doubled (H/Pt = 0.51). When the drying temperature is further increased, hydrogen chemisorption decreases. When the drying step is done under N_2 atmosphere, a marked decrease in H/Pt values occurs when the drying temperature exceeds 500°C.

3.3. Methylcyclohexane Dehydrogenation

MCH dehydrogenation was carried out at 300°C and atmospheric pressure, conditions favoring dehydrogenation, and no secondary reactions were observed by GC analysis. A test with monometallic Re/Al_2O_3 showed that the activity of Re for this reaction was at least two orders of magnitude lower than the activity of Pt in Pt/Al_2O_3 and Pt–Re/Al_2O_3. Thus, assuming structure insensitivity, the measured conversion depends on the Pt dispersion.

Figure 9 shows MCH conversion as a function of time on stream for Pt–Re/Al_2O_3 dried in air at different temperatures prior to reduction. The results show that the initial conversion and the conversion after 5 h are relatively independent of the drying temperature. This suggests that the actual Pt dispersion is not influenced by the drying temperature when the drying is done in air. Referring to

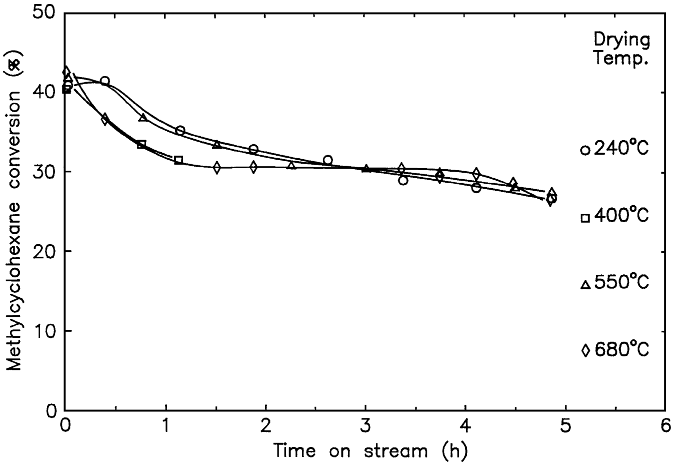

FIG. 9. Effect of drying temperature on methylcyclohexane dehydrogenation over Pt–Re/Al_2O_3 dried in air. Reaction conditions: 300°C, 1.1 bar, WHSV = 25 h^{-1}, and H_2/MCH = 40.

the H_2 chemisorption results, this shows that the lower H_2 chemisorption observed after low temperature pretreatment is not a result of low Pt dispersion. A large number of TEM micrographs of the Pt–Re/Al_2O_3 catalyst dried in air at 240°C showed no sign of metal crystallites larger than 10 Å (the detection limit of the TEM instrument).

The conversion of MCH as a function of time on stream after drying in N_2 is shown in Fig. 10. After drying at 240°C, the conversion profile is similar to that for drying in air, with an initial conversion of 40%. Drying temperatures of 550 and 680°C led to a significant decrease in MCH conversion indicating that the sintering process is accelerated at temperatures exceeding 500°C. From Fig. 10 it can be seen that the initial MCH conversion after N_2 treatment at 680°C is 30–40% lower than after low-temperature pretreatment at 240°C. However, after 3 h on stream the conversion after the 680°C treatment in N_2 is only 8% compared to 30% after treatment at 240°C. These results show that the sintered catalyst not only displays lower initial activity, but that deactivation also becomes more significant. As a probe for Pt sintering after high-temperature N_2 treatment, a catalyst sample was analyzed by TEM. Figure 11 shows a typical TEM micrograph for Pt–Re/Al_2O_3 dried in N_2 at 680°C. Indeed, metal crystallites were observed and can be found as black contours on the gray alumina background. The metal crystallite size was in the range of 20–50 Å. Some crystallites appeared to be of ordered structure having regular faces when pictured two dimensionally. As was outlined above; the very same catalyst pretreatment resulted in 30% lower initial conversion as compared to the low-temperature pretreatment.

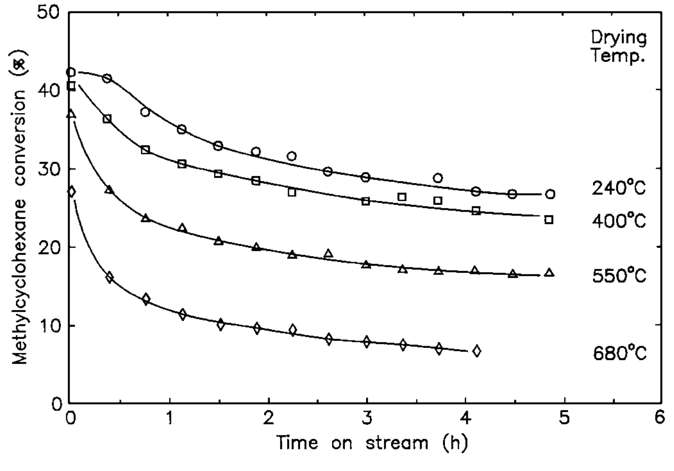

FIG. 10. Effect of drying temperature on methylcyclohexane dehydrogenation over Pt–Re/Al_2O_3 dried in N_2. Reaction conditions: 300°C, 1.1 bar, WHSV = 25 h^{-1}, and H_2/MCH = 40.

Figure 12 shows that the initial conversion of MCH dropped by 5 and 7% when 0.1 and 0.5 mol% H_2O were added to the H_2 gas stream during the reduction. Thus, water vapor lowers the Pt dispersion and the effect is dependent on the partial pressure of water. It is also evident from Fig. 12 that the decrease in the dehydrogenation activity with time on stream with H_2O present is more pronounced compared to the sample reduced in dry H_2.

3.4. *n-Heptane Conversion*

The conversion of *n*-heptane as a function of time on stream for Pt–Re/Al_2O_3 dried in air at 240–680°C is shown in Table 1. The conversion is about 95% and not very much affected by the drying temperature although a small increase with the drying temperature can be observed. The conversion was also very stable over the 40 h run, indicating a low rate of deactivation.

The results presented in Table 1 show that high selectivities (>80 mol%) of cracking products are observed while the selectivities of dehydrocyclization and isomerization are much lower. However, the selectivities are very dependent on the drying conditions applied prior to reduction. Drying at 240°C leads to 97 mol% cracking products. After drying at 550°C, the cracking selectivity is much lower

TABLE 1

Conversion and Product Distribution from the Reaction of *n*-Heptane on Pt–Re/Al_2O_3 Pretreated by Drying in Air

Drying temperature (°C)	*n*-Heptane conversion (%)	C_1/C_3 molar ratio	$S_{cracking}$ (C_1–C_6 paraffins) [mol%]	$S_{isomerization}$ ($iC_7 + iC_8$) [mol%]	$S_{dehydrocyclization}$ (C_{6+} aromatics) [mol%]
240	93.7	22	97.1	1.8	1.1
550	94.7	3.3	82.8	6.4	10.7
680	96.9	6.0	89.7	3.4	6.9

Note. Data obtained at 505°C, 16 bar, WHSV = 10 h^{-1}, and H_2/*n*-heptane = 10.

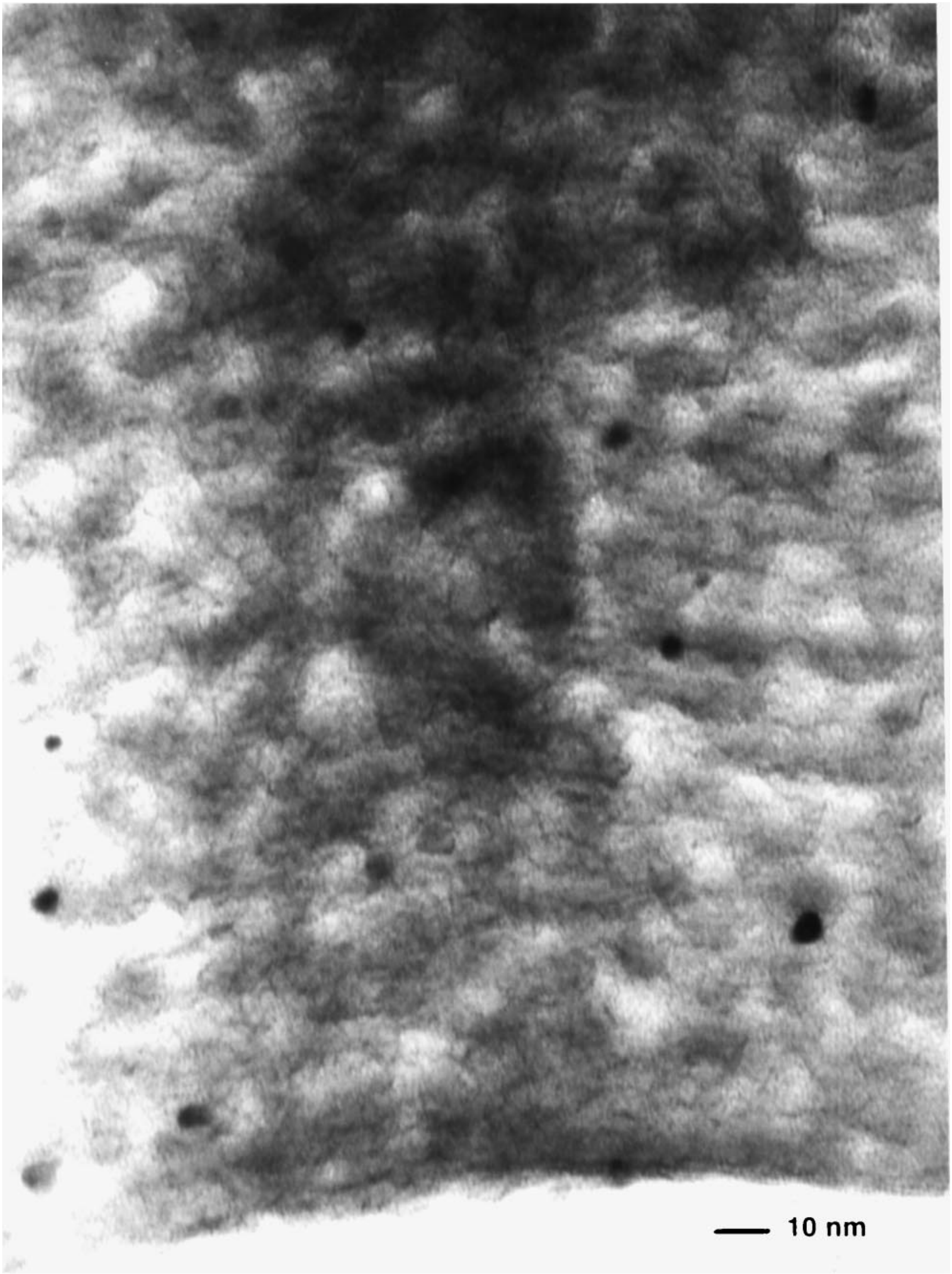

FIG. 11. Typical TEM micrograph of Pt–Re/Al$_2$O$_3$ dried in N$_2$ at 680°C for 4 h.

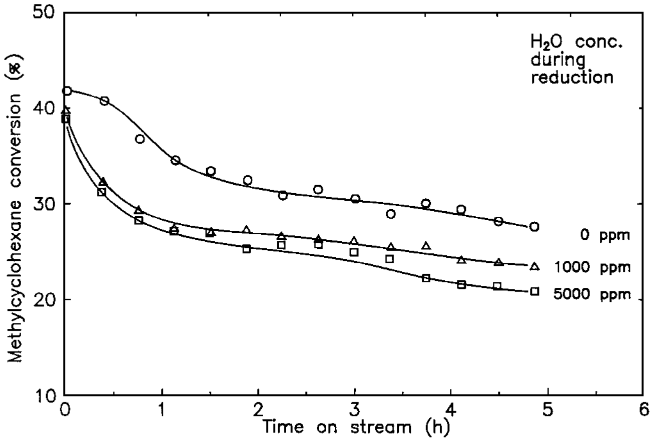

FIG. 12. Effect of H_2O (mol ppm) in the H_2 reduction gas during reduction of Pt–Re/Al_2O_3 for 1 h at 480°C on methylcyclohexane dehydrogenation. Catalyst pretreatment: 4 h drying in air at 550°C. Reaction conditions: 300°C, 1.1 bar, WHSV = 25 h^{-1}, and H_2/MCH = 40.

(83%) and isomerization and dehydrocyclization are more favored. The selectivity of cracking products increases again when the drying temperature is increased to 680°C.

The C_1/C_3 ratio can be used as an indicator of which type of cracking is dominating during the reaction. After low-temperature drying at 240°C, the C_1/C_3 ratio (Table 1) is 22, a very high value, indicating that hydrogenolysis prevails over-acid catalyzed cracking. The very high activity for hydrogenolysis is responsible for the high cracking selectivity shown in Table 1 while dehydrocyclization and isomerization suffers. After drying at 550°C, the C_1/C_3 value is only 3.3 showing a significant decrease in the hydrogenolysis activity.

4. DISCUSSION

4.1. *Pt/Al_2O_3*

The TPR results of Pt/Al_2O_3 (Fig. 1) are consistent with previous reports (10–14, 24–26). Generally, Pt/Al_2O_3 calcined in air at high temperature (500°C) is reduced at 250 to 300°C and often with a peak tail/shoulder or an additional peak near 450°C. The temperature of Pt reduction is set primarily by the calcination (oxidation) temperature, indicating that the commercial catalyst used in this work has been calcined at about 500°C. The H_2 consumption indicates that all Pt has an oxidation number of 4. However, the nature of the Pt species which are reduced in the two peaks is not obvious. The Pt/Al_2O_3 catalyst investigated contains chlorine. Lieske *et al.* (25) showed, using TPR and UV–VIS reflectance spectroscopy, that these catalysts form chloride-containing Pt surface complexes upon oxidation. Oxidation at 300°C resulted in formation of a $(Pt^{IV}(OH)_xCl_y)_s$ species, whereas oxidation at 500°C was found to produce a $(Pt^{IV}O_xCl_y)_s$ species (25). The reduction temperatures for these surface complexes were 260 and 290°C, respectively, which correlate well with the temperature of the first Pt peak in this work. Studies using both Cl-containing and Cl-free Pt/Al_2O_3 catalysts (13) also point to the formation of oxychlorided Pt species when Cl was present. It was shown, however, that for Cl-free catalysts, Pt oxide reduction occurred at temperatures similar to those of the chlorinated species but with lower hydrogen consumption. It was suggested that Cl-free Pt oxide is unstable and decomposition will occur even in O_2-containing atmospheres.

Regarding the reduction peak appearing close to 400°C it is generally assumed to be a Pt species interacting more strongly with the support. It has been shown (26) that this peak shifts toward a lower temperature when the Pt loading is decreased, suggesting increased metal support interaction. For the bimetallic Pt–Re catalyst (Fig. 2), this TPR peak disappears. Similar results were observed by Augustine and Sachtler (14), who suggested that the strong interaction of the Pt species with the support decreases in the vicinity of Re.

O_2 and H_2 chemisorption on Pt/Al_2O_3 (Fig. 6) is independent of the drying temperature when using air. O_2 chemisorption after N_2 treatment of monometallic Pt/Al_2O_3 at 500°C indicates that sintering occurs in the absence of O_2. The stoichiometry generally accepted for hydrogen chemisorption has been about 1.0. The measured H/Pt atomic ratio of 0.67 would therefore indicate that only two-thirds of the Pt atoms are available for chemisorption. However, it has been observed that chemisorption data are dependent on the experimental technique employed. Using static volumetric chemisorption, the H/Pt ratio is found to be 1.44 for otherwise similar experimental conditions. Such differences are likely related to the ability of the methods to detect weakly adsorbed species. The O/Pt value of 0.5 suggests that the chemisorption stoichiometry for O_2 is lower than for H_2. Kobayashi *et al.* (27) and Isaacs and Petersen (18) reported the ratio of chemisorbed oxygen to chemisorbed hydrogen, (O/Pt)/(H/Pt), to be 0.81 and 0.82, respectively. The value of (O/Pt)/(H/Pt) equal to 0.75 found in this work therefore seems reliable.

4.2. *Re/Al_2O_3*

The TPR profile of the Re/Al_2O_3 catalyst (Fig. 1) is in accordance with previous reports (10, 11, 14) showing a reduction temperature for Re in the range of 525 to 600°C for catalysts calcined at 500–525°C and Re was found to be almost completely reduced to the zero valent state. Augustine and Sachtler (14) found, however, that the degree of reduction decreased to 80% if the catalyst was treated in Ar at 500°C prior to reduction. Similar trends were also observed by Isaacs and Petersen (11). This has been explained by increased interaction with the alumina support as the catalyst is dehydrated. The present data show only 55% degree of reduction after low-temperature air treatment and indicate that the actual Re loading of our catalyst is lower than expected.

It has been shown using both chlorided catalysts (11) and chlorine-free catalysts (14) that the reduction temperature of Re is influenced neither by the drying temperature nor the presence of chlorine. The important factor seems to be the calcination temperature. After calcination at 500°C Re is in the +7 state as ReO_4 on a hydrated support and as a surface complex on a dehydrated support. In the presence of chlorine Malet *et al.* (13) suggest that these surface complexes could be oxychlorides, where the chlorine ligands strengthen the interaction and the anchoring of the Re species to the support.

In accordance with several studies (18, 28–30) we find that while both Pt and Re are capable of chemisorbing oxygen, only Pt chemisorbs H_2 under ambient conditions.

4.3. *Pt–Re/Al_2O_3*

4.3.1. Pt-catalyzed reduction of Re. TPR profiles of Pt–Re/Al_2O_3 dried in air (Fig. 2) correspond well with the results of Marecot *et al.* (15) which presented profiles of Pt–Re/Al_2O_3 dried in air at 120 and 450°C. One peak was observed after the low-temperature pretreatment, whereas three peaks (at 250, 360, and 520°C) were observed after air treatment at 450°C. Our results correspond with those of Marecot *et al.* (15) while Malet *et al.* (13) observed only two TPR peaks after drying Pt–Re/Al_2O_3 in air at 300 and 450°C. The consumption of H_2 during TPR after air treatment has generally been reported to correspond to a 90–100% degree of reduction, depending on the final TPR temperature. The two types of mechanisms proposed for the observed Pt-catalyzed reduction of Re after low-temperature drying suggest that the degree of hydration of the catalyst is responsible for the phenomenon. The observed weight loss during pretreatment (Fig. 5) may be explained in terms of surface dehydroxylation (14), dehydration of the Re oxide species (11), or by loss of capillary condensed water (16). All these phenomena are likely to proceed independently. From Fig. 5 it can be seen that there is no difference in the weight loss in air and N_2. This indicates that a different amount of water present in the case of N_2 and air is not the cause for the different TPR results.

The two mechanisms proposed for Re reduction are different at one important point: If the hydrogen spillover mechanism is valid, Pt and Re metal atoms will retain their positions on the catalyst surface after reduction, while the mechanism involving Re oxide migration leads to intimate contact and possibly alloy formation between Pt and Re. Indeed, on the basis of the chemisorption results and the hydrogenolysis activity measurements, alloy formation is likely to occur to various extents depending on drying conditions.

The large suppression of the H_2 adsorption (Fig. 8) observed after low drying temperature is taken as a further evidence for alloy formation. Both dehydrogenation measurements and TEM micrographs indicate high Pt dispersion after drying in air at 240°C so this is not caused by low Pt dispersion. H_2 chemisorption is likely suppressed due to fewer contiguous Pt atoms (required for dissociative chemisorption (18)) in the Pt–Re alloy crystallite. The results (Fig. 8) indicate that alloy formation decreases as the drying temperature is increased toward 550°C, but increases again as the drying temperature is increased. Further evidence for this trend is the measurement of the hydrogenolysis activity (C_1/C_3 ratios) during *n*-heptane conversion (Table 1). On this basis, a mechanism involving Re oxide migration is very likely.

The mobility of Re depends on the degree of catalyst hydration. However, at very high drying temperatures (>520°C) alloy formation increases although the catalyst is severely dehydrated. The observed loss of chlorine after high temperature pretreatment may induce increased mobility. Malet *et al.* (13) found, using TPR and hydrogenolysis measurements, that more alloy formation occurred on chlorine-free catalysts. It was concluded that Re oxide species are highly mobile in the abscence of chlorine for any degree of hydration of the alumina. Thus, the following mechanism of the Pt-catalyzed reduction of Re, depending on drying conditions, may be proposed:

—After drying at 240°C the catalyst is hydrated and the Re oxide species is mobile and migrates to reduced Pt which catalyzes its reduction, resulting in simultaneous reduction of Pt and Re at 300°C.

—After drying at 490°C the catalyst is less hydrated and the Re oxide species is less mobile requiring a higher temperature (375°C) in order to migrate to the Pt reduction centers. Part of the Re is immobile and is reduced at a reduction temperature characteristic of monometallic Re (550°C).

—A further increase in the drying temperature (>520°C) leads to further dehydration, but loss of chlorine induces increased mobility of the Re oxide species which can migrate to Pt reduction centers and be reduced at lower temperature (300–500°C).

4.3.2. Platinum dispersion in O_2 atmosphere. The platinum dispersion of the bimetallic catalyst was unaffected by drying temperatures up to 680°C in air atmosphere. The MCH dehydrogenation results (Fig. 9) are also clear. However, in that respect, these results do not correspond with previous studies of monometallic Pt/Al_2O_3 catalysts (36, 37), which show that oxidation temperatures exceeding 550°C leads to loss of chlorine and sintering of the platinum phase. The reason for this discrepancy is not obvious. In our study the heating in air to 680°C was done very carefully to minimize leaching of chlorine during the pretreatment (9% Cl loss) and this may be an important factor. The catalyst studied is a commercial sample and the preparation methods applied are likely also important.

4.3.3. Oxide decomposition and sintering in N_2 atmosphere. The reduction profiles of Pt–Re/Al_2O_3 after N_2 treatment (Fig. 3) agree well with published TPR profiles where Ar or He has been used as the drying atmosphere (11, 13, 14). As reported by Malet *et al.* (13), a marked decrease in the H_2 consumption is observed when increasing the drying temperature up to 450°C (Fig. 4). It was suggested that the higher H_2 consumption measured after low-temperature treatment could be ascribed to the reduction of carbon-containing impurities adsorbed on the catalyst, since CH_4 evolution during reduction was detected by mass spectroscopy. On the other hand, the same authors suggested that the low hydrogen consumption of their Pt/Al_2O_3 catalyst dried at 450°C was due to reduction (decomposition) of Pt during the pretreatment. The present results showing low TPR H_2 consumption after N_2 drying suggest that Pt decomposition might occur at low temperatures (<400°C) in an inert atmosphere. In fact, a detailed study of the catalyst color after N_2 drying supports this idea. The yellowish white, calcined fresh catalyst starts to change to gray when the temperature reaches 370°C (after 4 h treatment in N_2). When the temperature is further increased to 470°C, the dark gray color similar to that of a reduced sample appears. The same pattern for the change in color was observed also for Pt/Al_2O_3. No color change was observed after the same treatment in air.

Pt oxide decomposition has been reported to be accompanied by Pt sintering at temperatures exceeding 500°C (31). Both the O_2 chemisorption measurements (Fig. 7) and the methylcyclohexane dehydrogenation experiments (Fig. 10) and the TEM micrograph (Fig. 11) after N_2 drying strongly support this possibility. The results indicate that decomposition and sintering is likely to occur at temperatures of 400°C and higher. This process accelerates when the temperature exceeds 550°C. Thus a plausible decomposition reaction could be expressed as $(\mathrm{Pt}^{\mathrm{IV}}\mathrm{O}_x\mathrm{Cl}_y)_{\mathrm{surf.\ complex}} \rightarrow \mathrm{Pt}^0 + \mathrm{O}_2 + \mathrm{Cl}_2$. Chlorine analysis of fresh and pretreated catalysts indicate that drying temperatures exceeding 500°C leads to chlorine loss.

The TPR profile of Pt–Re after N_2 treatment at 650°C (Fig. 3) shows nearly no signal which could be ascribed to the reduction of Re, indicating that also Re decomposition occurs at high temperatures. An alternative cause for the results could be that Re in some way is trapped on the surface as difficult-to-reduce species due to some strong surface interaction, but this is not likely to occur since air pretreatment at the same temperature produces an easily reducible rhenium species.

4.3.4. Water vapor during reduction. The presence of water during reduction in H_2 is known to induce metal sintering (16, 32). From the MCH dehydrogenation measurements (Fig. 9), it is found that the amount of water on the catalyst prior to reduction, as set by the air drying temperature, has not influenced the dispersion of Pt on the Pt–Re catalyst. For catalysts dried at low temperature (240°C), the reduction involved heating the sample in dry H_2 from 240 to 480°C (2.4°C/min). It is evident from Fig. 5 that a considerable amount of water (ca. 1 wt%) will leave the catalyst during reduction. However, for the slow heating rate used during reduction, the rate of water release and the partial pressure of water will remain low.

Upon addition of 0.1 and 0.5 mol% water to the H_2 gas flow during reduction (Fig. 12) the Pt dispersion (as measured by methylcyclohexane dehydrogenation) was reduced considerably. The initial conversion dropped and the deactivation was more pronounced compared to the sample reduced in dry H_2. This may be explained by the ensemble size requirement for graphitic coke formation (33). Thus, the effect of water is dependent on the partial pressure. A water content of 0.1 mol% at 1.1 atm total pressure corresponds to 100 mol ppm H_2O in H_2 for an industrial unit operating at 10 bar and can be considered a relevant concentration industrially. The effect of water may be one of chlorine stripping, causing increased mobility of the Pt species—leading to sintering. Water may also induce hydration of a partly reduced complex, yielding a neutral Pt complex with high propensity for sublimation (16).

5. CONCLUSIONS

The present study demonstrates the importance of proper pretreatment of the metal function of Pt–Re/Al_2O_3 catalysts.

The degree of hydration of the catalyst prior to reduction, as defined by the drying temperature, strongly modifies the reducibility of rhenium and the extent of alloy formation in the reduced catalyst. When the catalyst is hydrated, Pt catalyzes the reduction of Re which is reduced at low temperature by a mechanism involving Re oxide migration. Alloy particles of Pt and Re are formed. When the catalyst is dehydrated, the Re oxide species is less mobile and requires higher reduction temperatures. A part of the Re present is immobilized and reduced at a temperature typical for monometallic rhenium. Less alloy formation does occur. If the catalyst is dechlorinated as for drying temperatures >520°C, Re oxide mobility increases, leading to more alloy formation.

An oxidizing atmosphere during pretreatment is preferable. Platinum dispersion is not affected at temperatures up to 680°C in air, while in N_2 platinum oxide decomposition and sintering are observed from temperatures of 400°C and higher. The presence of water vapor in the reducing gas also causes Pt sintering. The observed sintering increased at higher water vapor partial pressures.

O_2 and H_2 chemisorption measurements are valuable for determining the degree of rhenium reduction and the amount of alloy formation, rather than the metal dispersion.

ACKNOWLEDGMENT

Statoil is gratefully acknowledged for supporting this work.

REFERENCES

1. Kluksdahl, H. E., U.S. Patent 3,415,737 (1968).
2. Bertolacini, R. J., and Pellet, R. J., *in* "Catalyst Deactivation" (B. Delmon and G. F. Froment, Eds.), p. 73, Elsevier, Amsterdam, 1980.
3. Yermakov, Y. U., and Kuznetsov, B. N., *J. Mol. Catal.* **9**, 13 (1980).
4. Betizeau, C., Leclercq, G., Maurel, R., Bolivar, C., Charcosset, H., Frety, R., and Tournayan, L., *J. Catal.* **45**, 179 (1976).
5. Biloen, P., Helle, J. N., Verbeek, H., Dautzenberg, F. M., and Sachtler, W. M. H., *J. Catal.* **63**, 112 (1980).
6. Shum, V. K., Butt, J. B., and Sachtler, W. M. H., *J. Catal.* **96**, 371 (1985).
7. Ribeiro, F. H., Bonivardi, A. L., Kim, C., and Somorjai, G. A., *J. Catal.* **150**, 186 (1994).
8. Augustine, S. M., Alameddin, G. N., and Sachtler, W. M. H., *J. Catal.* **115**, 217 (1989).
9. Beltramini, J., and Trimm, D. L., *Appl. Catal.* **32**, 71 (1987).
10. Wagstaff, N., and Prins, R., *J. Catal.* **59**, 434 (1979).
11. Isaacs, B. H., and Petersen, E. E., *J. Catal.* **77**, 43 (1982).
12. Mieville, R. L., *J. Catal.* **87**, 437 (1984).
13. Malet, P., Munuera, G., and Caballero, A., *J. Catal.* **115**, 567 (1989).
14. Augustine, S. M., and Sachtler, W. M. H., *J. Catal.* **116**, 184 (1989).
15. Marecot, P., Peyrovi, M., and Barbier, J., *C. R. Acad. Sci. Paris. Ser. II* **307**, 1509 (1988).
16. Barbier, J., Bahloul, D., and Marecot, P., *J. Catal.* **137**, 377 (1992).
17. Jossens, L. W., and Petersen, E. E., *J. Catal.* **76**, 265 (1982).
18. Isaacs, B. H., and Petersen, E. E., *J. Catal.* **85**, 1 (1984).
19. Isaacs, B. H., and Petersen, E. E., *J. Catal.* **85**, 8 (1984).
20. Bond, G. C., *J. Mol. Catal.* **81**, 99 (1993).
21. Lemaitre, J. L., *in* "Characterization of Heterogenous Catalysis" (F. Delannay, Ed.), Dekker, New York, 1984.
22. Prestvik, R., Ph.D. Thesis, Norwegian Institute of Technology, Trondheim, 1995.
23. Weast, R. C. (Ed.), *in* "Handbook of Chemistry and Physics," 67th ed., CRC Press, Boca Raten, FL. 1986.
24. McNicol, B. D., *J. Catal.* **46**, 438 (1977).
25. Lieske, H., Lietz, G., Spindler, H., and Völter, J., *J. Catal.* **81**, 8 (1983).
26. Chen, L., Ni, Y., Zang, J., Lin, L., Luo, X., and Cheng, S., *J. Catal.* **145**, 132 (1994).
27. Kobayashi, M., Inoue, Y., Takahashi, N., Burwell, R. L., Butt, J. B., and Cohen, J. B., *J. Catal.* **64**, 74 (1980).
28. Bolivar, C., Charcosset, H., Frety, R., Primet, M., Tournayan, L., Betizeau, C., Leclercq, G., and Maurel, R., *J. Catal.* **45**, 163 (1976).
29. Freel, J., *Prepr. Am. Chem. Soc. Div. Petrol. Chem.* **18**, 10 (1973).
30. Yao, H. C., and Shelef, M., *J. Catal.* **44**, 392 (1976).
31. Yao, H. C., Sieg, M., and Plummer, H. K., Jr., *J. Catal.* **59**, 365 (1979).
32. Sushumna, I., and Ruckenstein, E., *J. Catal.* **109**, 433 (1988).
33. Sachtler, W. M. H., *J. Mol. Catal.* **25**, 1 (1984).
34. Shum, V. K., Butt, J. B., and Sachtler, W. M. H., *J. Catal.* **99**, 126 (1986).
35. Pieck, C. L., Marecot, P., Querini, C. A., Parera, J. M., and Barbier, J., *Appl. Catal. A: Gen.* **133**, 281 (1995).
36. Lee, T. J., and Kim, Y. G., *J. Catal.* **90**, 279 (1984).
37. Anderson, J. A., Mordente, M. G. V., and Rochester, C. H., *J. Chem. Soc. Faraday Trans. 1* **85**(9), 2983 (1989).