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THERMAL BEHAVIOUR OF NH_4ReO_4 SUPPORTED ON INORGANIC GELS

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Abstract

Results of TG and DTA studies as well as an analysis of the liberated gas products have led us to recognize differences in the mechanisms of transformations taking place in the systems NH_4ReO_4/Al_2O_3–SiO_2 (25 wt% SiO_2 and NH_4ReO_4/Al_2O_3 containing 1.1, 3.3 and 3.3, 9.9, 17.8 wt% NH_4ReO_4. Thermal decomposition of NH_4ReO_4 on the supports used begins with release of ammonia, which is strongly bound with the surface in the system of 3.3 wt% NH_4ReO_4/Al_2O_3, and undergoes oxidation to nitrogen oxides in the air atmosphere. In the other systems studied, the process of ammonia release starts already at 473 K and ammonia does not get oxidized. Moreover, it has been established that ammonia perrhenate supported on the surface of Al_2O_3–SiO_2 in the amount of 1.1 or 3.3 wt% undergoes partial thermal decomposition to ReO_2 which is further oxidized in the air atmosphere. As follows from the thermal studies as well as the measurements of activity in a reaction of 1-hexene metathesis, the active centres of the reaction of olefin metathesis are formed on the surface of the studied systems after their calcination at 473 K.

Keywords: 1-hexene metathesis, TG/DTA analyses, thermal decomposition of NH_4ReO_4 on Al_2O_3 and Al_2O_3–SiO_2

Introduction

Thermal decomposition of ammonia perrhenate supported on appropriate inorganic gels is one of the stages in production of heterogeneous rhenium-based catalysts of olefine metathesis reactions. The temperature of the thermal decomposition, the kind of support used as well as the amount of rhenium supported on its surface essentially affect the activity and stability of the obtained catalysts

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[1–3]. The studies of rhenium-based catalysts performed so far have provided extensive information on the structure of the surface rhenium-based species which are precursors of the active centres of olefine metathesis reaction. The studies also covered the properties of functional (OH) groups present on the surface of the inorganic gels, which are also involved in formation of these active centres [3–6].

The aim of this work was to study the transformations taking place on the surface of the system: NH_4ReO_4/inorganic gel upon heating in temperatures from 293 to 1373 K, which effected generation of the active centres of olefine metathesis reaction.

Experimental

Samples

The NH_4ReO_4/inorganic gel systems were prepared by pore volume impregnation of the inorganic gel with calculated amounts of an aqueous solution of ammonium perrhenate (MZPiP-Plock), followed by drying overnight at 383 K in air for 16 h. Inorganic gels used as the supports were α-alumina (Ketjen CK 300, 80–250 μm) and silica-alumina (Akzo SA-HA, 25 wt% Al_2O_3, 180–250 μm).

Thermal analysis

Thermogravimetric (TG) and differential thermal (DTA) analyses were conducted using a Shimadzu TGA-50(H)/A50 thermoanalytic network system. The conditions of the TG and DTA measurements were as follows: temperature interval: 273–1373 K, heating rate: 5 K min^{-1}; specimen weight: about 20 mg; nitrogen or air flux: 100 cm^3 min^{-1}. Powdered α-alumina was used as a reference material.

Gas determination methods

Analysis of gases liberated on heating the studied systems in the atmosphere of air and nitrogen was performed by the discontinuous method in temperatures ranging from 293 to 973 K. Ammonia was detected with Nessler reagent and assayed by standard titration (0.1 *M* HCl) [7]. Nitrous oxides converted to stable derivatives by diphenylamine were determined by visible spectrophotometry [7].

Metathesis of 1-hexene

The catalyst used in this study was obtained by annealing the 3.3 wt% $NH_4ReO_4/Al_2O_3–SiO_2$ system at various temperatures within the range 373–873 K. The weight percentage of the catalyst was nominal, calculated from the amounts of compounds used for the preparation. The annealing was conducted either in the air atmosphere for 2 h and then for 1 h in (purified of moisture and oxygen) nitrogen or in nitrogen only. After calcination the catalyst was introduced into the stirred glass batch reactor under dried nitrogen. The whole reaction was carried out in the liquid phase at room temperature (293±2 K) in nitrogen atmosphere with 0.1 g of a catalyst.

The use of a non-polar solvent (heptane, 2 cm^3) and a cocatalyst (Et_4Pb), provided the optimal reaction conditions.

The heptane and 1-hexene were purified of moisture and oxygen by treatment with surface Mn(II)/silicagel and distilled under argon prior to use. The usual molar ratios were Pb:Re=1:1, 1-hexene:Re=500:1. The course of the reaction was followed by taking small samples (0.01 cm^3) at suitable times, from which again amounts of 1 μl were used for GC analysis (1.5×3 column packed with 5% OV-101 on Chromosorb WHAW, 373 K). Conversion of 1-hexene was determined on the basis of the percentage content of 1-hexene in the products of the reaction.

Results and discussion

NH_4ReO_4/Al_2O_3–SiO_2 system

The relative changes in the mass of the system NH_4ReO_4/Al_2O_3–SiO_2, containing 1.1 or 3.3 wt% NH_4ReO_4, taking place during the annealing in air are illustrated in Fig. 1. The curves in this figure are obtained by subtraction of the

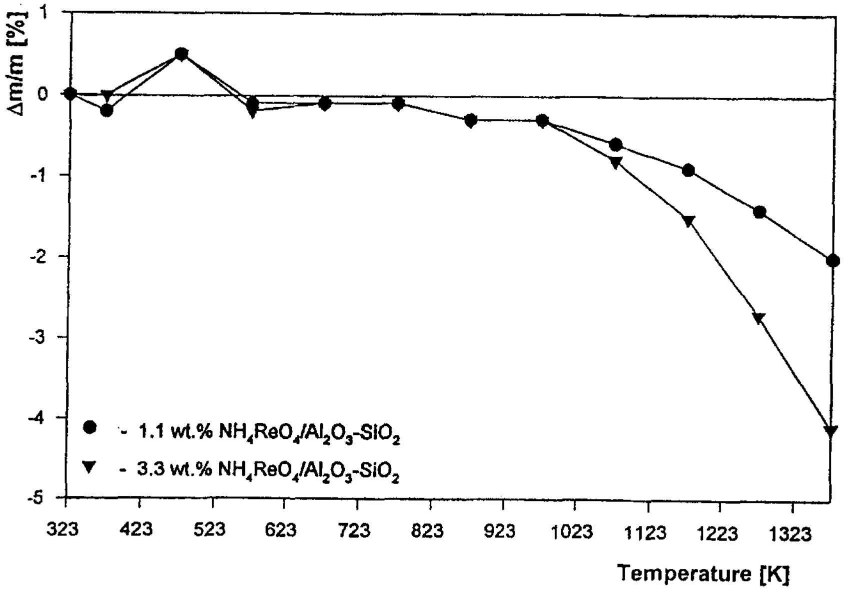


Fig. 1 Relative changes of mass (%) as a function of the temperature of annealing

thermogravimetric curve of the support from the relevant curves obtained for the studied systems, taking into account the content of the support in a given system. This way of presentation of the results provides the possibility of deriving the most accurate information about the changes caused by the presence of ammonia perrhenate on the support surface. The course of the thermogravimetric curves shown in Fig. 1 is similar. In both cases a small increase of the relative mass of the system was observed reaching a maximum at 473 K and then its relative mass slowly decreased. With further increase of the annealing temperature, this mass decrease becomes more profound reaching 2.0 and 4.1% for the systems containing 1.1 and 3.3 wt% of ammonia perrhenate.

The results of differential thermal analysis (DTA) expressed per a unit of mass ($\Delta T/m$) for the systems containing 1.1 or 3.3 wt% of NH_4ReO_4 as well as for the support (Al_2O_3–SiO_2) alone, are given in Fig. 2. The character of DTA curves recorded for all samples indicates thermal effects in the support which can evidently be ascribed to the processes of dehydration (I-minimum) and dehydroxylation (II-minimum) [8]. Starting from 323 K, the value of $\Delta T/m$ increases and reaches a maximum at about 550 K. The value of $\Delta T/m$ at the maximum is almost the same for the pure support and the system containing 3.3 wt% of NH_4ReO_4. As follows from a comparison of the curves shown in Fig. 2, the system containing 1.1 wt% of NH_4ReO_4 in the temperature range 473–673 K is characterized by less pronounced thermal effects. This suggests that the processes occurring in this system produce weaker thermal effects than

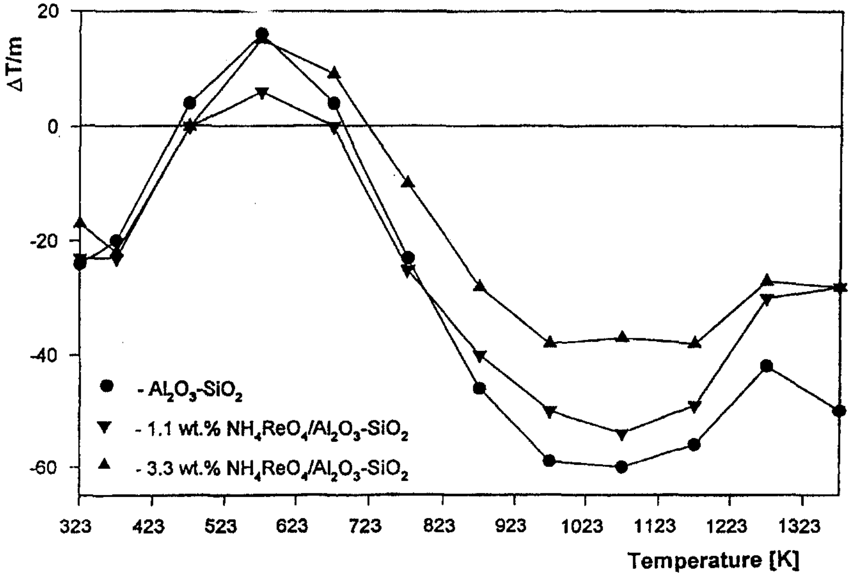


Fig. 2 Changes in the temperature difference per a unit of mass ($\Delta T/m$) as a function of temperature of annealing

those taking place in the support. An increase in NH_4ReO_4 concentration above 1.1 wt% strengthens the exothermal effect. In higher temperatures, the exothermal effects in the systems containing rhenium are stronger than those observed for pure support. For the system containing 3.3 wt% of NH_4ReO_4 this is true already at 573 K whereas for the system with 1.1 wt% of NH_4ReO_4 at 773 K.

The system $NH_4ReO_4/\gamma-Al_2O_3$

The curves illustrating relative changes of the mass of $NH_4ReO_4/\gamma-Al_2O_3$ system containing 3.3, 9.9 or 17.8 wt% NH_4ReO_4, taking place upon annealing in the air atmosphere are shown in Fig. 3. For the system with 3.3 wt% of NH_4ReO_4, its relative mass rather substantially decreases with increasing temperature of annealing and at 673 K this decrease reaches 7.5%. Then, with a further increase in temperature of annealing, from 673 to 1173 K, the relative mass decreases slowly and then falls abruptly for temperatures higher than 1173 K. The course of the curve describing the behaviour of the system containing 9.9 wt% of NH_4ReO_4 is completely different. With temperature increasing up to 473 K, the relative mass increment is 1.7% which means that the support mass decrement is greater than the mass decrement of the system. With a further increase in the temperatures of annealing, the relative mass decrement slowly decreases and starting from 1173 K it becomes equal to that observed for the support alone. Annealing at still higher temperatures is accompanied by a fast decrease in the mass decrement of the system which reaches 4.0% at 1373 K. The curve describing the behaviour of the system with 17.8 wt% of

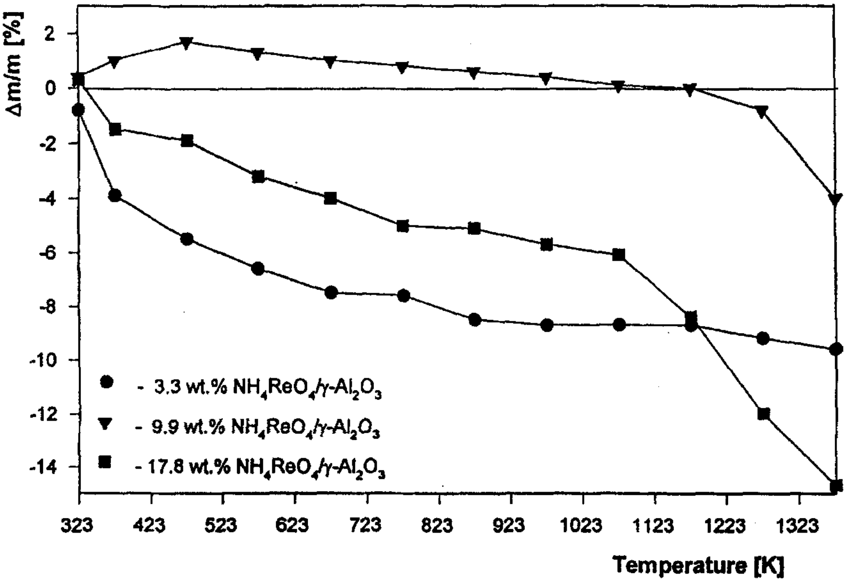


Fig. 3 Relative changes of mass (%) as a function of the temperature of annealing

NH_4ReO_4 testifies to a monotonous decrease of the relative mass decrement. In the range 473–873 K it is rather slow and starting from 1073 K it becomes faster, reaching 14.7% at 1373 K. Similarly as in the case of the system $NH_4ReO_4/Al_2O_3-SiO_2$, the changes in thermal effects of NH_4ReO_4 supported on $\gamma-Al_2O_3$ are mostly related to the effects of the support. As follows from the curves presented in Fig. 4 and describing the behaviour of the systems with 9.9 and 17.8 wt% of NH_4ReO_4, the thermal effects in these systems are weaker than those exhibited by the support.

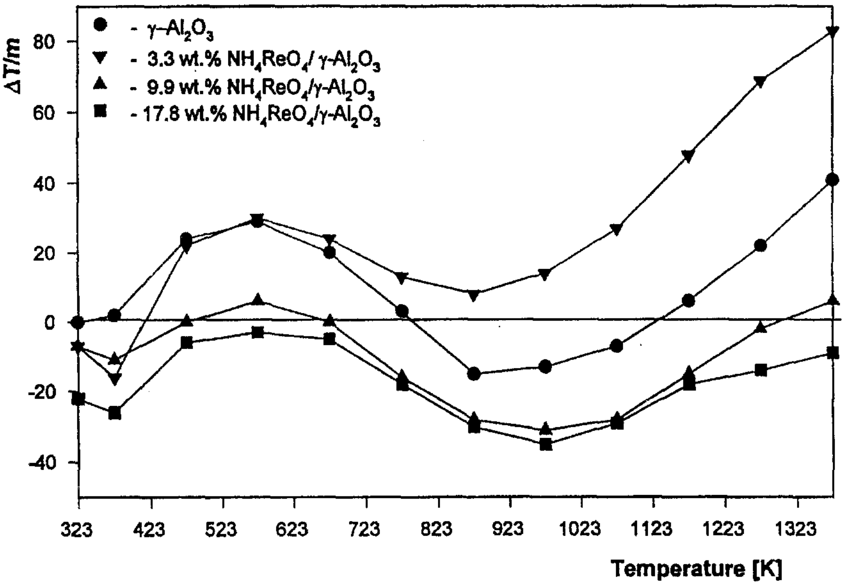


Fig. 4 Changes in the temperature difference per a unit of mass ($\Delta T/m$) as a function of temperature of annealing

The DTA results expressed per a unit of mass ($\Delta T/m$) determined for the sample containing 3.3 wt% NH_4ReO_4 in temperatures below 473 K indicate that the values of the thermal effects are lower than those for the pure support. Above 673 K the course of DTA curves indicates a strong exothermal effect in the samples containing rhenium.

The effect of the gas atmosphere over the sample on the processes occurring during annealing

Annealing of the studied systems from room temperature to 1373 K at a fixed rate of temperature increase resulted in liberation of volatile products whose quality and quantity dependent on the chemical composition of a studied system, the kind of atmosphere over the sample and the temperature of annealing. The reactions of decomposition were accompanied by a change in the colour of the studied samples which testifies to the formation of different species of rhenium on the surface of grains of the applied inorganic gels.

During annealing of the sample containing 3.3 wt% of NH_4ReO_4 supported on γ–Al_2O_3 in the nitrogen atmosphere in temperatures up to 873 K, no decomposition products other than water were observed. During annealing in higher temperatures trace amounts of ammonia were detected in the volatile products of decomposition. When the system was annealed in the air atmosphere, the products of decomposition contained water, and above 673 K also nitrogen oxides. The grains of the system remained white independently of the kind of atmosphere and temperature.

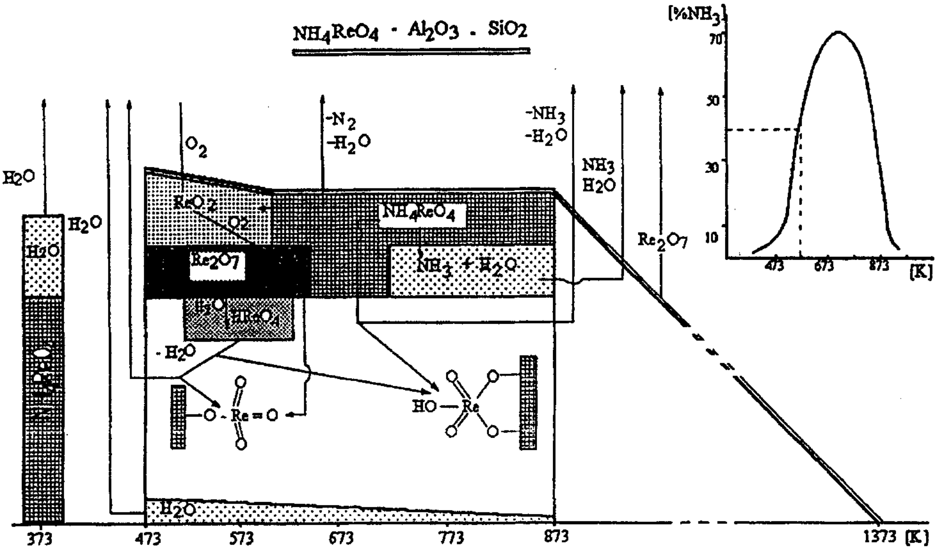


Fig. 5 Transformations of NH_4ReO_4 on Al_2O_3–SiO_2

Independently of the atmosphere (air nitrogen), the gas products of decomposition of NH_4ReO_4 supported on Al_2O_3–SiO_2 revealed the presence of steam (water vapour) and above 473 K also ammonia (Fig. 5). The amount of the gas ammonia relative to the mass of NH_4ReO_4 varied from 10 to 70% depending on the rate and temperature of heating. The maximum amount of gas ammonia was detected in the temperatures 673–723 K. No nitrogen oxides were determined in the gas products of decomposition of these samples. The samples heated in the atmosphere of nitrogen above 673 K turned black whereas those heated in air remained white. The gas products of the systems with 9.9 and 17.8 wt% of NH_4ReO_4 supported on γ–Al_2O_3 evolved from 473 K revealed the presence of ammonia.

Catalytic studies

The samples obtained by annealing the system 3.3 wt% NH_4ReO_4/Al_2O_3–SiO_2 at 373, 473, 573, 673, 773 ad 873 K for 2 h in the air atmosphere, then for 1 h in the nitrogen atmosphere, and next activated with Et_4Pb were subjected to catalytic studies. The results of the catalytic activity in the model reaction of metathesis 1-hexene (1) of this system annealed at different temperatures are collected in Table 1.

$$\text{1–hexene} \overset{\text{cat.}}{\rightleftharpoons} \text{ethene} + \text{5–decene} \quad (1)$$

Catalytic conversion of 1-hexene in the presence of catalysts obtained by annealing of 3.3 wt% NH_4ReO_4/Al_2O_3–SiO_2 system only under nitrogen atmosphere at 473 and 673 K reaches 39.8 and 65.4%, respectively. These experiments were all performed at room temperature. Results of the studies show that annealing of the above system at a temperature as low as 473 K, irrespective of the surrounding atmosphere, leads to generation of the active centres of the metathesis reaction. Moreover, it is not necessary to oxidize the rhenium compounds on the surface of the support in order to initiate the active centres. In general, the catalytic activity of the studied systems increases with increasing temperature at which a given system was annealed.

Table 1 Metathesis reaction of 1-hexene initiated by 3.3 wt% NH_4ReO_4/Al_2O_3–SiO_2/Et_4Pb system annealed at various temperatures. The reaction temperature: 293 K

Temp. of annealing/K	373	473	573	673	773	873
Conversion/%	0	41.4	67.7	71.0	78.7	80.8

Variations of mass of NH_4ReO_4 supported on inorganic gels

The studies performed so far indicate that the rhenium species formed on the surface of the alumina gel become mobile and undergo sublimation in temperatures above 1173 K, in particular when the systems contain relatively large amounts of NH_4ReO_4. The rhenium species supported on aluminium-silica gels reveal mobility starting from 823 K, and above this temperature they undergo sublimation [3, 6]. The observed rapid decrease in the relative mass decrement for the systems NH_4ReO_4/Al_2O_3–SiO_2 at 973 K and for NH_4ReO_4/Al_2O_3 in the range 1073–1173 K, confirms the above findings. The values of the relative mass decrement at 1323 K for the NH_4ReO_4/Al_2O_3–SiO_2 systems containing 1.1 and 3.3 wt% of NH_4ReO_4 are 2.0 and 4.1 wt%, respectively, (Fig. 1), hence they are higher than the amount of NH_4ReO_4 added to the systems during the preparation, which suggests that rhenium species have been totally removed from the support during calcination. However, the mass decrements recorded at the same temperature for NH_4ReO_4/alumina gel indicate that some rhenium species still remain bound to the support. As follows from the curves describing mass changes of the systems liberating ammonia, the beginning of the mass decrement decrease coincides with the moment the ammonia release starts. This means that the rhenium species forming with release of ammonia from NH_4ReO_4, bound water stronger than the support. This in turn inhibits desorption of water from the surface of the system grains, and water is stronger adsorbed by the surface of the system than ammonia. This process is particularly well seen for the system containing 9.9 wt% of NH_4ReO_4 on alumina gel. A different behaviour has been observed for the system 3.3 wt% $NH_4ReO_4/\gamma-Al_2O_3$. The gas products released on its thermal decomposition do not include ammonia and the system liberates relatively large amounts of water. A similar difference in the amount of the water adsorbed in the system $NH_4ReO_4/\gamma-Al_2O_3$ depending on the amount of the supported NH_4ReO_4, has been observed in IR measurements [9]. The mass change of the pure support on heating is due to desorption of physically bound water and in higher temperatures also gradual dehydroxylation of the surface. In the case of systems with ammonia perrhenate, the mass decrements are due to desorption of water physically adsorbed by the support and removal of water introduced during impregnation. The effects observed in higher temperatures are a consequence of dehydroxylation of the system surface and sublimation of rhenium species. The dehydroxylation of the system surface may involve formation of surface rhenium species with participation of the surface OH group of the support.

Thermal transformations of NH_4ReO_4 supported on inorganic gels

According to literature data [10, 11], thermal decomposition of ammonia perrhenate may lead to formation of products of different quality and in different quantities depending on the temperature and atmosphere of the process. Its slow thermal decomposition begins at 473 K and leads to formation of amorphous oxides which with the temperature increasing from 550 to 670 K undergo almost total decomposition to ReO_2, according to the equation:

$$NH_4ReO_4 \rightarrow ReO_2 + H_2O + 0.5N_2 \qquad (2)$$

The formed rhenium dioxide in low temperatures occurs in the hydrated form of black colour while in higher temperatures it undergoes transformation to anhydrous oxide of dark red colour. In the range 473–663 K the gas products of NH_4ReO_4 decomposition were found to contain only nitrogen and water, however, in higher temperatures also traces of ammonia were detected which indicates that a parallel side reaction:

$$2NH_4ReO_4 \rightarrow Re_2O_7 + 2NH_3 + H_2O \qquad (3)$$

occurred.

With increasing temperature of the decomposition taking place in the air atmosphere, the formed ReO_2 is oxidized to tri- ($T \approx 623$ K), penta-, hexa- and volatile white-yellow heptoxide dirhenium ($T > 723$ K) [12, 13]. The above transformation is evidenced on the DTA curve by an endothermal peak with the maximum at 663 K whereas the exothermal peak at 700 K and the exothermal peak in the range 873–923 K correspond to phase transitions [13].

The DTA and TG curves describing thermal decomposition of ammonia perrhenate supported on Y zeolite reveal a peak at 500 K, ascribed to a large mass decrement caused by removal of 90% of water. Further mass decrement noted in the range 573–623 K is interpreted as a consequence of release of ammonia [12].

The above presented literature data provide some, but not comprehensive, explanation of the results obtained in this work. Release of ammonia from the studied systems upon heating suggests the thermal decomposition of NH_4ReO_4 according to reaction (3). It has been established [2] that the decomposition of NH_4ReO_4 described by this reaction occurs only above 663 K and is a side reaction, whereas in the systems studied in this work it has evidently been the main reaction. The release of ammonia observed already at 473 K indicates that reaction (3) must be catalyzed by the surface of the applied inorganic gel supports. Moreover, the behaviour of ammonium perrhenate supported on zeolite reported in [12] can also be explained by a catalytic process. The appearance of black grains of the support when the system is heated in the nitrogen atmosphere above 573 K, suggests the formation of ReO_2 which in the air atmosphere is oxidized to Re_2O_7 [14], which is evidenced on the DTA curve by an exothermal peak. Re_2O_7 formed as a product of reaction (3) and as a consequence of oxidation of the product of reaction (2) can, in certain temperatures, lead to generation of the catalytic centres of the reaction of olefin metathesis, on the surface of the studied systems [3, 4, 6].

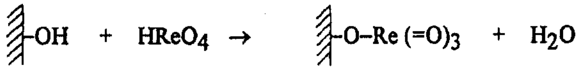
The formation of the centres active in olefin metathesis established in the studied systems at 473 K cannot be related to the reaction of Re_2O_7 with the stretched $\equiv$Si–O–Si$\equiv$ bridges since they do not exist at that temperature [16]. Moreover, the Lewis acid centres which could be formed as a results of the gel surface dehydration also cannot exist at that temperature on the surface of the studied systems. Those which could have possibly be formed would be saturated with water and the gel surface, especially its pores, would be covered with a thin layer of water [16]. The formation of the active centres of olefin metathesis at 473 K should be interpreted as due to the catalysed reaction (3) since at this temperature thermal decomposition of the unsupported NH_4ReO_4 itself does not occur. The formed Re_2O_7 can create active centres in a reaction with hydroxyl groups, but most probably it also reacts with the water adsorbed on the support surface for to give perrhenate acid. This process can explain the observed decrease in mass decrement of the studied systems at that temperature. If reaction (3) was not catalyzed at 473 K and thus did not occur, the active centres in olefin metathesis could only be formed in result of direct interaction of ammonium perrhenate with the hydroxyl groups present on the gel surface, however, then ammonia should be released.

Ammonia can also be released as a result of decomposition of NH_4^+ cation whose presence can be due to dissociation of ammonium perrhenate. In water environment NH_4^+ cation can be decomposed already at 373 K, however at that temperature no release of ammonia from water solutions of NH_4ReO_4 is detected [14]. This indicates that this cation must be strongly stabilized in such solutions by the perrhenate anion. It is possible that such stabilization does not occur already at 473 K or that the perrhenate anion enters into a reaction with the surface and does not stabilize NH_4^+ any more.

According to the obtained results, the thermal decomposition of ammonium perrhenate on the surface of alumina-silica gel at 473 K, involves liberation of ammonia. A similar process of decomposition can occur with NH_4ReO_4 on the surface of Al_2O_3. In the case of system of 3.3 wt% $NH_4ReO_4/\gamma-Al_2O_3$, the ammonia released upon heating is strongly bound to the surface and undergoes oxidation, similarly as the ammonia bonded with the surface hydroxyl groups of the zeolites. Such bonded ammonia gets oxidized above 700 K which is evidenced by a strong exothermal effect or undergoes desorption above 873 K when the annealing is conducted under the helium atmosphere [16].

The other systems made of alumina gel and greater amounts of NH_4ReO_4 (9.9 and 17.8 wt%) do not reveal the property of strong binding of ammonia.

Not excluding any of the above presented possible ways of formation of the catalytic centres of the metathesis reaction considered, on the basis of the literature data and the results obtained in this study, we can propose the following schemes of these centres formation:



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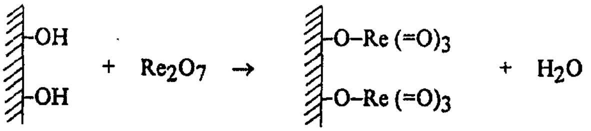
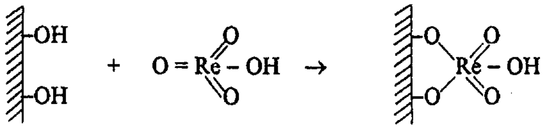


(5)

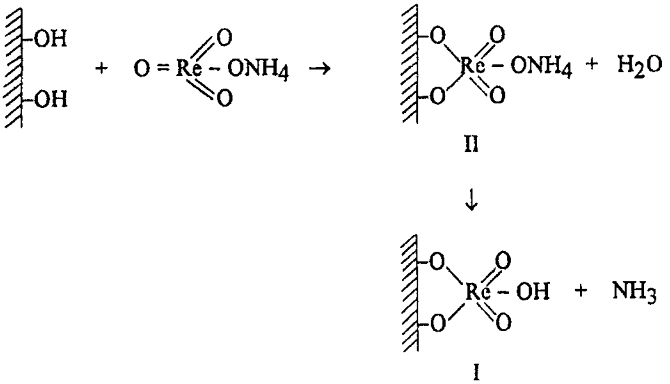
The product of the above reactions are tetrahedral surface rhenium species of C_{3v} symmetry with three terminal Re=O bonds [5].

The above mentioned surface rhenium species having two terminal Re=O bonds (determined by IR-spectra) [5] can be formed as a product of a reaction analogous to the acetal reaction i.e the one of CH_3ReO_3 with dioles [17]. In the case of perrhenate acid such an interaction can be described by the following scheme:



(6)

whereas for ammonium perrhenate by:



(7)

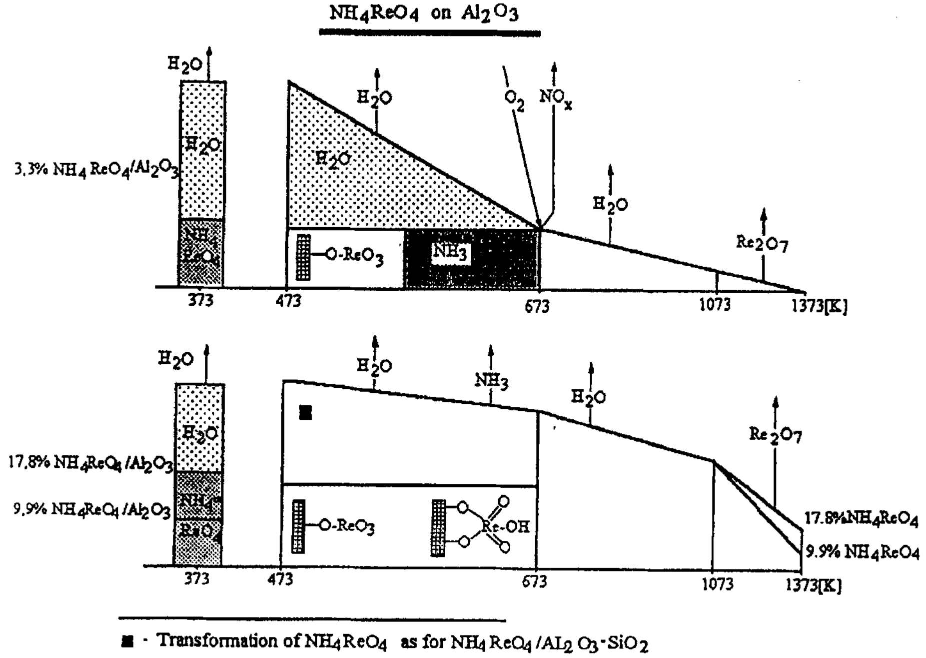


Fig. 6 Transformations of NH_4ReO_4 on γ–Al_2O_3

As follows from the above schemes, the rhenium species containing ONH_4 group, denoted as species II, should undergo decomposition to species I, accompanied by release of ammonia. The surface rhenium species of C_{3v} symmetry appear on the surface of alumina gel when the system contains no more than 6 wt% of Re_2O_7 [5], so the observed weak binding of water should be ascribed to them. The exothermal effects observe upon calcination of the systems $NH_4ReO_4/Al_2O_3-SiO_2$ are difficult to explain. Most probably, the relatively greater thermal effects recorded for the systems with 3.3 wt% of NH_4ReO_4 starting from 600 K, can be interpreted as a consequence of the initiated process of ReO_2 oxidation (ReO_3 is formed already at 623 K). The thermal effects positive relatively to those exhibited by the support, observed above 900 K, can be accounted for by the oxidation of the surface rhenium species to Re_2O_7, which later undergoes sublimation from the surface. Figures 5 and 6 present schematically all the processes and reactions described above taking place during calcination of the studied systems. The upper lines in the diagrams illustrate the change of the system mass during calcination. Figure 5 shows also the amount of liberated NH_3 during calcination of the 3.3 wt% $NH_4ReO_4/Al_2O_3-SiO_2$ system.

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