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FT-IR Spectroscopic Studies of NH_4ReO_4 Supported on Inorganic Gels

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Results of IR study of the systems NH_4ReO_4/Al_2O_3 and NH_4ReO_4/Al_2O_3-SiO_2 heated in the range 293–723 K are given. The systems contained rhenium in amounts corresponding to those in typical heterogeneous catalysts of olefin metathesis. The IR absorption spectra, recorded for the wavelengths 1700–1300 cm^{-1}, enabled detection of adsorption at the Brönsted and Lewis type acid centres of water and ammonia, released during thermal decomposition of ammonium perrhenate. The spectra indicated a similarity between the adsorption centres present on the surface of the systems 17.8 wt.% NH_4ReO_4/Al_2O_3 and 3.3 wt.% NH_4ReO_4/Al_2O_3-SiO_2 and those on the surface of the systems 3.3 and 9.9 wt.% NH_4ReO_4/Al_2O_3. The presence of adsorption centres in the former systems should be related to the phase of the surface rhenium species, while in the latter the centres occur on the surface of the support.

Key words: heterogeneous rhenium catalyst, FT-IR

To establish the mechanism of generation of the active centres for olefin metathesis in heterogeneous rhenium catalysts, the changes in the systems NH_4ReO_4/Al_2O_3 and NH_4ReO_4/Al_2O_3-SiO_2 were studied by the DTA and DTG methods between 293 and 1400 K. The results revealed different pathways of the systems transformation depending on the amount of rhenium deposited and the kind of support. The transformations lead to formation of surface rhenium species of different structure [1,2].

To supplement the hitherto studies, the systems were subjected to IR spectroscopic analysis, whose results allowed identification of the surface centres of adsorption of water and ammonia and the form in which they occur at the surface. It was established that the molecules of ammonia and water appear as a result of thermal decomposition of ammonium perrhenate and dehydration of the surface of the supports used.

EXPERIMENTAL

The NH_4ReO_4/inorganic gel systems were prepared by pore volume impregnation of the inorganic gel with appropriate amounts of an aqueous solution of ammonium perrhenate (MZRiP-Płock – analytical reagent grade), followed by drying at 423 K in air for 16 h. The inorganic gels used as supports were: alumina prepared by hydrolysis of alumina isopropoxide and silica-alumina (Akzo HA, 24.3 wt.% Al_2O_3, 180–250 μm). All samples after drying were ground in a mortar and pressed into transparent pellets, which were placed in an IR cell equipped with heaters allowing their calcination to 723 K. IR measurements were performed in a quartz cell connected with a simple vacuum system (10^{-1} Pa). To protect the sample in the IR cell from moisture and CO_2 we applied the Aeronex Gate Keeper. Also the chamber in the FTIR spectrometer with the IR cell was washed by high purity He. The saturation of pellets surface with probing molecules (NH_3, H_2O) was performed at room temperature by introducing 5 mmol of probing substance into the cell evacuated to a pressure of 10^{-1} Pa. The process of saturation took 0.5 hour. After this time the cell was degassed again to a pressure of 10^{-1} Pa. After 3-hour calcination at a given temperature, the pellets were cooled to room temperature and their transmission IR spectrum (250 scans) was recorded on a Bruker IFS88 FTIR spectrometer. Mainly, the spectra were recorded for the wavenumbers 1700–1300 cm^{-1}.

The following systems were studied: H_2O adsorbed on the carriers: Al_2O_3 and Al_2O_3-SiO_2; NH_3 adsorbed on the carriers: Al_2O_3 and Al_2O_3-SiO_2; 3.3; 9.9 and 17.8% wt. NH_4ReO_4 supported on Al_2O_3; 3.3% wt. NH_4ReO_4 supported on Al_2O_3-SiO_2, all annealed at 373, 473, 573, 673 and 723 K for 3 hs.

RESULTS AND DISCUSSION

IR transmission spectra of the thermally treated (in the range from 293 to 723 K) systems NH_4ReO_4/Al_2O_3 and NH_4ReO_4/Al_2O_3-SiO_2 were recorded in the range 4000–500 cm^{-1}. The spectra reveal broad and very intense bands in the range 3760–2200 cm^{-1}, assigned to stretching vibrations of the O–H and N–H bonds of the adsorbed molecules of water and ammonia, and bands in the range below 1300 cm^{-1}, assigned to the oxygen bridges M–O–M (M = Si, Al) formed on the surface of the supports studied. In the range 1700–1300 cm^{-1} positions and intensity of observed bands were dependent on the composition of the system and the temperature of its calcination. These bands were attributed to the deformation vibrations of the O–H and N–H bonds in the molecules of water and ammonia adsorbed at the Lewis and Brönsted type acid centres and to some molecules attached to the support surface through physical forces [3,4]. Thus, the observation of changes in this range should allow an interpretation of conversions taking place on the surface of the systems studied upon their calcination.

The following absorption bands were identified in the spectra recorded: – the band at 1680 cm^{-1}, which disappears at 473 K and appears for a few samples calcined at 673 K, assigned to the presence of hydrated -ONH_4 group [5,6]; – the bands in the range 1644–1600 cm^{-1}, assigned to the molecules of water or ammonia adsorbed on strong the Lewis type acid centres (perturbed by other adsorbed species) [4,6,7]; – the bands in the range 1580–1570 cm^{-1}, assigned to the molecules of water and ammonia adsorbed on the Lewis type acid centres [7]; – the band at 1464 cm^{-1}, assigned to the presence of the amide structure of ammonia bound to aluminium ions [6]; – the bands in the range 1440–1420 cm^{-1}, assigned to ammonia adsorbed on the Brönsted type acid centres (surface salt – ONH_4) [4–7]; – the band at about 1414 cm^{-1} attributed to the ammonium group of ammonium perrhenate [8]; – the bands below 1400 cm^{-1}, attributed to the ammonia adsorbed on weak Lewis acid sites and aluminium perrhenate formed, while thermal decomposition of supported NH_4ReO_4 [6].

The systems studied contained 3.3, 9.9 and 17.8 wt. % NH_4ReO_4 deposited on alumina gel and 3.3 wt. % NH_4ReO_4 deposited on the silica-alumina gel. According to literature, in the first two systems surface rhenium species appearing as a result of calcination do not form a monolayer, while such a monolayer fully covers the support surface of the latter two systems [9,10]. In order to identify the species adsorbed on the surface of the supports used and on the monolayer of rhenium species the absorption spectra of the supports with the adsorbed molecules of water and ammonia were recorded. The samples of pure supports were calcined in the same range of temperatures as the preparations studied.

The system H_2O/Al_2O_3: The absorption bands appearing in the IR spectra of the system H_2O/Al_2O_3 calcined in 373–673 K and their assignment to particular molecules adsorbed at particular centres are given in Table 1 and in Fig. 1a. Increasing the temperature of calcination of the alumina gel studied leads to the disappearance of the band at 1640 cm^{-1}, for the samples calcined already at 573 K. Simultaneously, the intensity of the bands at 1600 and 1470 cm^{-1} increases with increasing temperature of calcination to 573 K. These bands disappear for the sample calcined at 673 K, the spectrum of which shows only an inflection point at 1570 cm^{-1}. However, the weak inflection point observed at 1600 cm^{-1} in the spectra of samples calcined in lower temperatures becomes pronounced in the spectrum of the sample calcined at 673 K. Moreover, in this spectrum a very intense band appears at 1480 cm^{-1}.

These bands are assigned to the molecules of water adsorbed at the acid centres of the gel studied. The strength of the centres and the temperature of their formation can be inferred from the bands that appeared in the spectra of the samples calcined at low temperatures and then disappeared in the spectra of the samples calcined at high temperatures.

Table 1. Absorption bands observed in IR spectra of H_2O and NH_3 adsorbed on Al_2O_3 after calcination at different temperatures.

Temp. (K)	IR bands (cm^{-1})				Dominant molecules
			H_2O/Al_2O_3		
	H_2O/OH	H_2O/LA_S			
473	1640 s	1600 m	1570 m	1470 w	H_2O/OH H_2O/LA_S
573	–	1600 s	1570 s	1470 w	H_2O/LA_S

Temp. (K)	IR bands (cm^{-1})								Dominant molecules
				NH_3/Al_2O_3					
	$O\text{-}NH_4$	H_2O, NH_3/LA_S	$AlNH_2$	$O\text{-}NH_4$	NH_3-f	NH_3/LA_W			
473	–	1570 s	1460 s	–	–	1342 w	–	1270 m	$H_2O/NH_3/LA_S$, NH_3/LA_W, $AlNH_2$
573	1680 w	1580 s	1460 s	1440 b	–	1342 w	–	1270 w	NH_3/LA_S, $AlNH_2$

H_2O/OH – water bound to surface -OH groups
LA_s – strong Lewis type acidic centre
s – strong band, b – inflection point, m – medium strong band, w – weak band
LA_w– weak Lewis type acidic centres
f – physically adsorbed

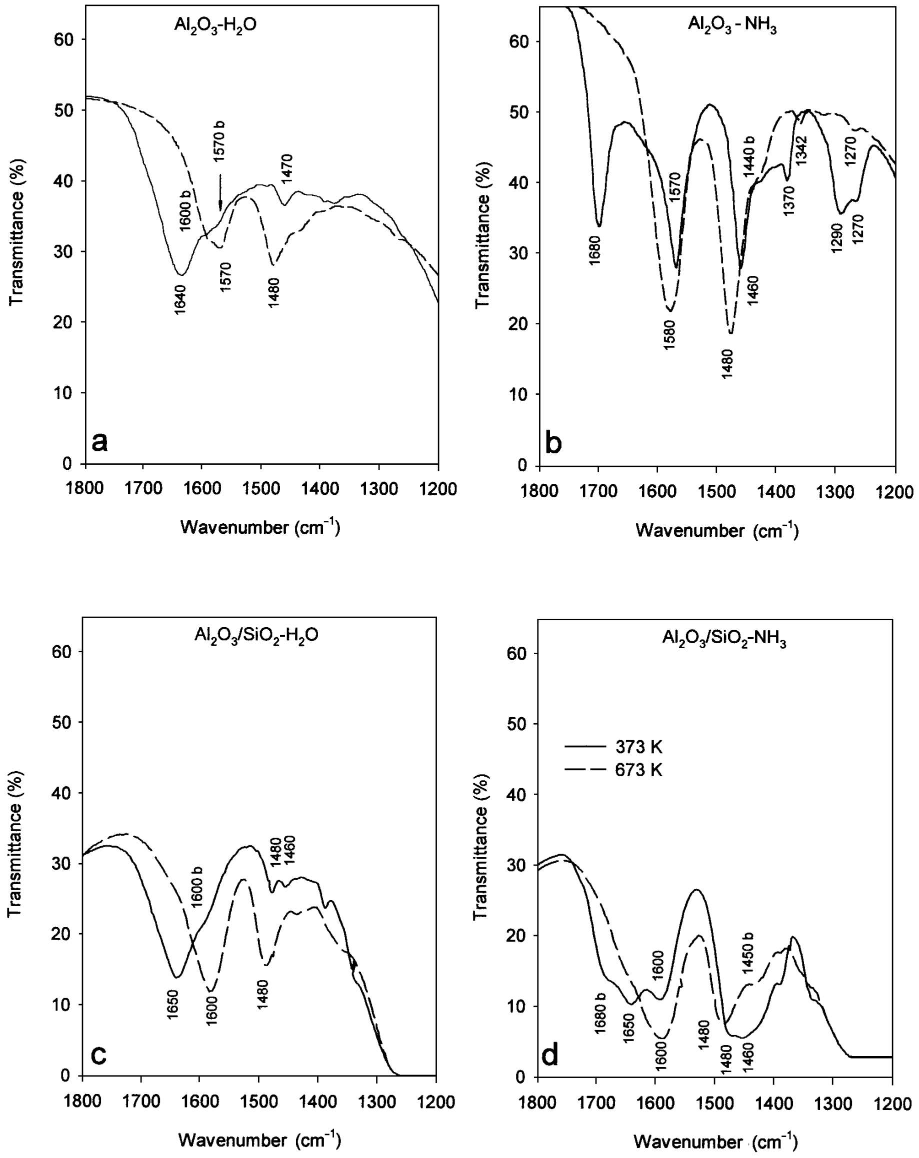

Figure 1. FT-IR spectrum of: (a) H_2O/Al_2O_3, (b) NH_3/Al_2O_3, (c) H_2O/Al_2O_3-SiO_2 and (d) NH_3/Al_2O_3-SiO_2 systems calcined *in situ* at 373 K (—) and 673 K (-----), respectively.

At low temperatures the surface of the alumina gel is covered by -OH groups forming a monolayer [11]. Thus, the band at 1640 cm^{-1} should be assigned to the molecules of water hydrogen-bonded to this monolayer of -OH groups [11]. This way of bonding of water molecules on the alumina gel surface dominates up to 473 K. Apart from the water bonded in this way there are relatively few water molecules bonded at the Lewis type acid centres (such centres are deshielded aluminium ions). The vibrations of these water molecules can be responsible for the bands at 1600, 1570 and 1470 cm^{-1}. Increases in the calcination temperature cause desorption of hydrogen-bonded water and a gradual dehydroxylation of the gel surface. This process leads to formation of Lewis type acid centres, which adsorb water molecules, and that is why in the absorption spectra of the samples calcined up to 573 K the intensity of the bands at 1600 and 1470 cm^{-1} increases. The disappearance of these bands in the spectrum of the sample calcined at 673 K and the appearance of new relatively intense bands at 1570 and 1480 cm^{-1} indicates the formation of new Lewis type acid centres at this temperature and a simultaneous disappearance of those occurring in the sample calcined at 573 K.

The system NH_3/Al_2O_3: It should be expected that on the surface of the system NH_3/Al_2O_3 calcined at 373 K the molecules of water and ammonia will be mainly bonded through hydrogen bonds with the monolayer of the surface OH groups. The IR spectrum of this system is shown in Fig. 1b, while the wavenumbers at which the bands occur are given in Table 1. Analysis of the absorption bands suggests that the molecules of ammonia form the $-ONH_4$ salt with the OH groups of the gel surface and, as indicated by a relatively intense band at 1680 cm^{-1}, these salts are complexed by the water molecules on the surface of the system.

The excessive water and ammonia are complexed by aluminium ions, which is concluded from the presence of the relatively intense band at 1570 cm^{-1}. The presence of the bands at 1370, 1290 and 1270 cm^{-1} suggests that part of the molecules of ammonia involved in complexes occur at the Lewis type acid centres and part becomes physically adsorbed on the support surface.

In the spectrum of the system NH_3/Al_2O_3 calcined at 473 K the band at 1680 cm^{-1} does not occur, which means that the weak hydrated ammonium salts decompose at this temperature. The above description of the conversions is consistent with literature data [5,6]. The ammonia released in the process is bonded at the Lewis type centres that also bound water, so the intensity of the band at 1570 cm^{-1} increases.

An increase in the intensity of the band at 1460 cm^{-1}, assigned to the amide group $-NH_2$ at the simultaneous disappearance of the $-ONH_4$ groups, suggests that the amide group is formed during decomposition of the surface ammonium salt as a result of its dehydration:

$$=Al-ONH_4 \rightarrow =Al-NH_2 + H_2O$$

In the IR spectrum of the sample calcined at 573 K the band at 1680 cm^{-1} and the bands assigned to the presence of the molecules of ammonia bonded at the Brönsted and Lewis type acid centres appear again. The shift of the band at 1570 cm^{-1} to 1580 cm^{-1} indicates that at that temperature dehydration of the gel surface generates new acid centres including those of Brönsted type at which ammonia is adsorbed.

The shift of the band at 1570 cm^{-1} suggests that the water adsorbed in lower temperatures at the Lewis type centres has been in higher temperatures exchanged by ammonia. Therefore, at 673 K ammonia dominates on the surface of the system. It is mostly bonded at the Lewis acid centres and in amide groups.

The system Al_2O_3-SiO_2/H_2O: The IR spectrum of the system Al_2O_3-SiO_2/H_2O calcined at 373 K shows an intense band at 1650 cm^{-1} and relatively low intense bands at 1600, 1480 and 1450 cm^{-1} (see Table 2 and Fig. 1c).

Table 2. Absorption bands observed in IR spectra of H_2O and NH_3 adsorbed on Al_2O_3-SiO_2 system after calcination at different temperatures.

Temp. (K)	IR bands (cm^{-1})					Dominant molecules
	H_2O/Al_2O_3-SiO_2					
	H_2O/OH	H_2O/LA_S	H_2O/LA_S	H_2O/LA_W		
473	1650 s	1600 w	1480 m	–		H_2O/OH
573	1650 b	1600 s	1480 m	–		H_2O/LA_S
	NH_3/Al_2O_3-SiO_2					
	ONH_4	H_2O/OH	H_2O, NH_3/LA_S	H_2O/LA_S	ONH_4	
473	–	–	1600 s	1480 s	1450 b	H_2O/LA_S, H_2O, NH_3/LA_S
573	–	–	1600 s	1480 s	1450 b	H_2O/LA_S, H_2O, NH_3/LA_S

An increase in the temperature of calcination leads to the disappearance of the band at 1450 cm^{-1} in the spectrum of the sample calcined at 473 K and the band at 1650 cm^{-1} in the spectrum of the sample calcined at 573 K. Simultaneously, the intensity of the bands at 1600 and 1480 cm^{-1} increases. Thus, these bands can be assigned to the deformation vibrations of the water molecules complexed at strong Lewis type centres present on the surface of Al_2O_3-SiO_2 gel. The bands at 1650 and 1450 cm^{-1} are assigned to the deformation vibrations of the water molecules hydrogen-bonded to the monolayer of -OH groups on the gel surface.

A notable increase in the intensity of the band at 1600 cm^{-1} in the spectra of samples calcined at lower temperatures contrasted with the increase of the intensity of the band at 1480 cm^{-1}, suggests that the adsorption centres responsible for the band at 1650 cm^{-1} are generated at the first stage of dehydration of the gel studied. Their interaction is responsible for the appearance of the band at 1480 cm^{-1}.

The system NH_3/Al_2O_3-SiO_2: The IR spectrum of the system NH_3/Al_2O_3-SiO_2 calcined at 373 K reveals bands of relatively low intensity at 1680 and 1460 cm^{-1}, which can be assigned to hydrated surface groups -ONH_4 [4,5] (see Table 2 and Fig. 1d).

The last band observed (*e.g.* at 1450 cm^{-1}) is probably superimposed on the band assigned to the vibrations of water molecules bonded to weak Brönsted type acid centres. The bands disappear in the spectrum of the sample calcined at 473 K. The spectrum of the sample calcined at 373 K reveals the bands assigned to adsorbed water analogous to those noted for the system H_2O/Al_2O_3-SiO_2, and the band at 1600 cm^{-1} is more intense. This suggests that the band is complex and includes also the bands assigned to the ammonia adsorbed. The spectra of the samples of NH_3/Al_2O_3-SiO_2 calcined at higher temperatures show only the bands at 1600 and 1480 cm^{-1}. The desorption of ammonia above 473 K suggests that these bands originate from the vibrations of the water molecules bonded at strong Lewis type acidic centres, similarly as it was for the system H_2O/Al_2O_3-SiO_2.

The system 3.3 wt.% NH_4ReO_4/Al_2O_3: Analysis of the spectra of the systems H_2O/Al_2O_3 and NH_3/Al_2O_3 calcined at different temperatures permitted identification of the molecules on the surface of the system 3.3 wt.% NH_4ReO_4/Al_2O_3 and the centres at which they are bound (see Table 3).

Table 3. Absorption bands observed in IR spectra of the 3.3, 9.9 and 17.8 wt.% NH_4ReO_4/Al_2O_3 systems after calcination at different temperatures.

Temp. (K)	IR bands (cm^{-1})							Dominant molecules
				3.3 wt.% NH_4ReO_4/Al_2O_3				
	H_2O/OH	NH_3/LA_S	$AlNH_2$	O-NH_4	NH_4ReO_4	NH_3/LA_W		
473	1641 s	1580 b	1464 w	1423 w	–	1395 w	1375 w	H_2O/OH
573	1641 m	1580 b	1464 m	1430 b	–	1395 w	1375 w	H_2O/OH, $AlNH_2$
673	1641 b	1580 s	1464 s	1430 b	–	1395 w	1375 w	NH_3/LA_S, $AlNH_2$
				9.9 wt.% NH_4ReO_4/Al_2O_3				
	ONH_4	H_2O/OH	NH_3/LA_S	$AlNH_2$	ONH_4	NH_3/LA_W		
473	–	1633 b	1543 s	1464 m	1423 b	1375 w		NH_3/LA_S
573	–	1634 w	1575 s	1464 s	1423 b	1378 w		NH_3/LA_S, $AlNH_2$
673		1634 b	1575 s	1464 s	1423 b	–		NH_3/LA_S, $AlNH_2$
				17.8 wt.% NH_3ReO_4/Al_2O_3				
	ONH_4	H_2O/LA_S	NH_3/LA_S	$AlNH_2$	ONH_4	NH_4ReO_4	NH_3/LA_W	
473	–	1627 s	1573 b	1464 w	1423 w	–	1395 w	H_2O/LA_S
573	–	1627 s	1573 b	1470 m	1423 w	–	–	H_2O/LA_S
673	–	1620 s	1573 b	1464 m	1423 w	–	–	H_2O/LA_S

After calcination at 373 K there are molecules of water and ammonia bonded to the surface -OH groups, as indicated by the bands at 1641 and 1525 cm^{-1}, and molecules of ammonia physically bound to the surface of the system. The presence of these forms of ammonia testifies that the interaction of ammonium perrhenate with the gel surface has started already at that temperature with simultaneous liberation of the gas product, which is bonded by the surface of the system. The presence of the absorption band at 1402 cm^{-1} indicates that ammonium perrhenate introduced onto its surface has not totally reacted. At this temperature also ammonium salts $-ONH_4$ appear on the surface of this system, which testifies the presence of acidic -OH groups. These $-ONH_4$ groups are a result of ammonium perrhenate conversion taking place in these conditions (see Table 3). The increase of temperature of calcination leads to a gradual appearance of water and ammonia molecules bound to strong Lewis type acidic centres and to a formation of amide groups $=Al-NH_2$. At 723 K only the molecules of ammonia bound to the strong Lewis type acidic centres and amide groups are present on the surface of the samples studied. The fact that the ammonia is strongly bonded explains why its desorption is not visible [1]. A few exemplary bands appearing in IR spectra of this system calcined at 293 and 723 K assigned to the molecules occurring on its surface are given in Fig. 2a.

The system 9.9 wt.% NH_4ReO_4/Al_2O_3: The spectra of the system 9.9 wt.% NH_4ReO_4/Al_2O_3 recorded at RT indicate the presence of the following groups on its surface: hydrated ammonium salts $-ONH_4$, ammonia physically bound to the surface, trace amounts of amide groups and water molecules bonded to the -OH groups on the surface of the system. However, the band assigned to these water molecules is shifted to 1633 cm^{-1} by 8 cm^{-1} lower than the corresponding value observed for the system 3.3 wt.% NH_4ReO_4/Al_2O_3 (see Table 3). The intensity of the band decreases with increasing temperature of calcination of the systems studied. The disappearance of the surface ammonium salts with increasing temperature of calcination is accompanied by an increase in the amount of ammonia bonded at strong Lewis type centres as well as at -OH acidic groups with formation of amide species. The ammonia bonded in the form of amide groups is prevalent on the surface of this system at 723 K. Some exemplary absorption bands assigned to the molecules occurring on the surface of the system at 293 and 723 K are shown in Fig. 2b.

The system 17.8 wt.% NH_4ReO_4/Al_2O_3: As revealed by the IR absorption spectra of the system 17.8 wt.% NH_4ReO_4/Al_2O_3 calcined at selected temperatures, the molecules of water bonded at the strong Lewis type acidic centres dominate on its surface, irrespective of the temperature of the system calcination. The position of the band assigned to these water molecule changes slightly, from 1634 to 1620 cm^{-1}, with increasing temperature of calcination, however, no changes in its intensity were noted. Apart from the water molecules bonded in this way, there are also small amounts of ammonium salts $-ONH_4$ and amide groups $-NH_2$ (Table 3). Moreover, at RT there are ammonium perrhenate and hydrated forms of ammonium salts on the surface of this system. A few exemplary absorption bands appearing in the IR spectra of the species occurring on its surface at 293 and 723 K are shown in Fig. 2c.

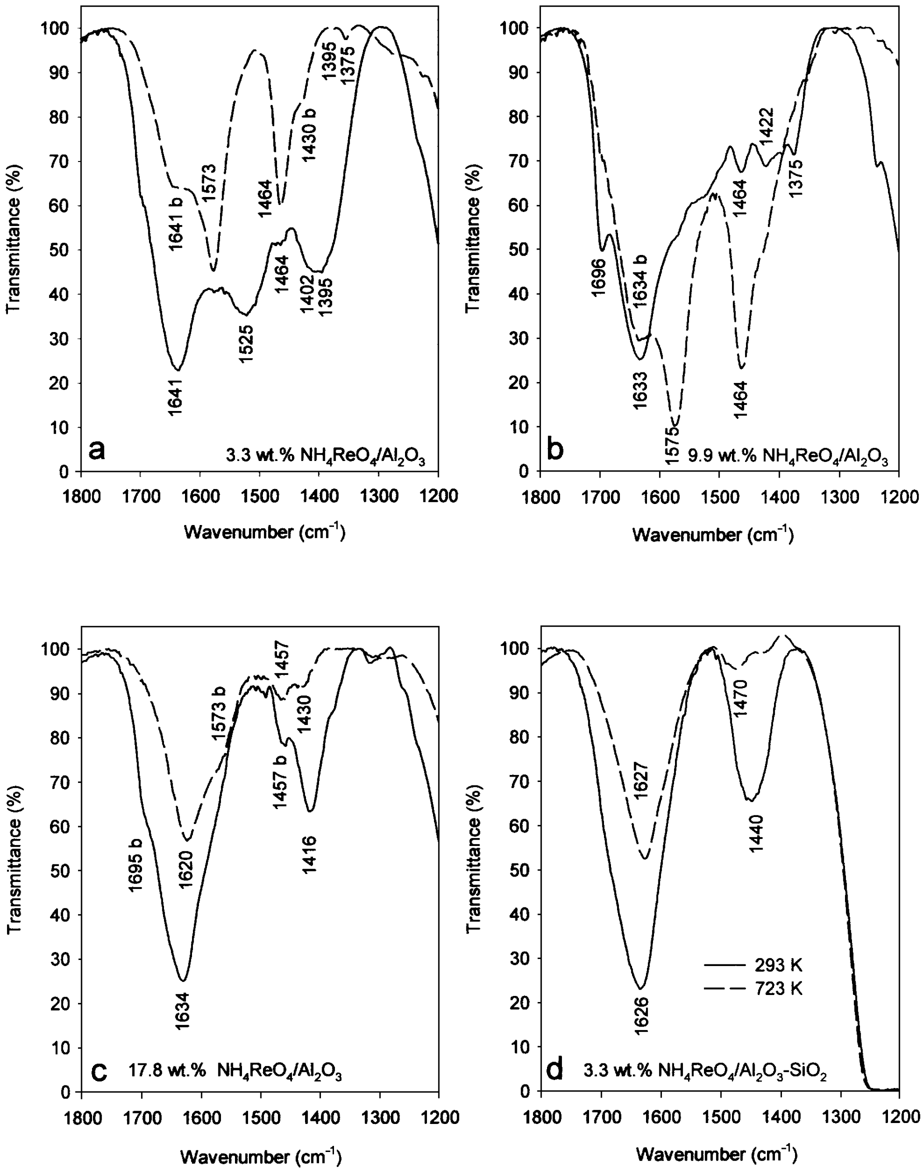

Figure 2. FT-IR spectrum of: (a) 3.3 wt.% NH_4ReO_4/Al_2O_3, (b) 9.9 wt.% NH_4ReO_4/Al_2O_3, (c) 17.8 wt.% NH_4ReO_4/Al_2O_3 and (d) 3.3 wt.% NH_4ReO_4/Al_2O_3-SiO_2 systems thermally treated *in situ* at 293 K (—) and 723 K (-----) , respectively.

The system 3.3 wt.% NH_4ReO_4/Al_2O_3-SiO_2: The IR absorption spectra of the system 3 wt.% NH_4ReO_4/Al_2O_3-SiO_2 calcined at temperatures up to 723 K indicate the presence of water molecules adsorbed at strong Lewis type centres on its surface, analogously as for the system 17.8 wt.% NH_4ReO_4/Al_2O_3. Apart from this surface species, dominant up to 673 K, there are also the -ONH_4 salts (see Table 4). At 723 K only water molecules occur on the surface of this system.

Table 4. Absorption bands observed in IR spectra of the 3.3 wt.% NH_4ReO_4/Al_2O_3-SiO_2 system after calcination at different temperatures.

Temp. (K)	IR bands (cm^{-1}) H_2O/LA_S	 H_2O/LA_S	 ONH_4	Dominant molecules
293	1626 s	–	1440 m	H_2O/LA_S, ONH_4
473	1626 s	–	1440 m	H_2O/LA_S, ONH_4
573	1627 s	–	1440 m	H_2O/LA_S, ONH_4
673	1627 s	1470 w	1440 w	H_2O/LA_S
723	1627 s	1470 w	–	H_2O/LA_S

Exemplary absorption bands in the IR spectra of the molecules on the surface of this system at 293 and 723 K are shown in Fig. 2d. The systems with a large number of surface species, calcined at relatively low temperatures, in particular those containing 3.3 and 9.9 wt.% of ammonium perrhenate deposited on alumina gel, have only few surface species at 723 K. Examples of the species occurring on the surface of the systems studied calcined above 673 K are given in Table 5.

The data from Table 5 indicate that ammonia bound at the strong Lewis type acid centres and in amide species is dominant on the surface of the systems 3.3 and 9.9 wt.% NH_4ReO_4/Al_2O_3. This way of bonding ammonia prevents its desorption from the surface of these systems up to 773 K (see Table 3). The water molecules present in the systems calcined up to 673 K undergo complexation at strong Lewis type acid centres. If we assume that the position of the bands assigned to the water bound in this way is determined by the structure of the centres, we can infer that these centres are similar on the surface of alumina and alumina-silica gels. According to literature data, these centres are aluminium cations [11]. The Lewis type acid centres occurring on the surface of the systems 17.8 wt.% NH_4ReO_4/Al_2O_3 and 3.3 wt.% NH_4ReO_4/Al_2O_3-SiO_2 should be characterized by a similar structure but different from that of the centres present on the surface of the supports used. The literature data indicate that the surface of the two systems is covered with a monolayer of rhenium species [10]. These rhenium species are formed as a result of the reaction of ammonium perrhenate or products of its thermal decomposition with hydroxyl groups of the gels studied. In the aluminium gel support the first to react are the basic and then acidic groups. As follows from the IR study, on the surface of the systems with ammonium perrhenate up to about 10% the reaction runs only with the involvement of the basic -OH groups [12]. On the silica-alumina gel studied the -OH groups are strongly acidic [13].

Table 5. Absorption bands of dominant species on the investigated systems after calcination at 673 K.

System	IR bands (cm^{-1})				
	H_2O/LA_S	H_2O/LA_S	NH_3/LA_S	H_2O/LA_S	$AlNH_2$
3.3 wt.% R/Al_2O_3*			1573 s		1464 s
9.9 wt.% R/Al_2O_3	1634 b		1575 s		1464 s
17.8 wt% R/Al_2O_3	1620 s		1573 w		1457 w
3.3% wt R/Al_2O_3-SiO_2	1627 s			1470 w	
H_2O/Al_2O_3-SiO_2		1600 s		1480 s	
NH_3/Al_2O_3-SiO_2		1600 s		1480 s	
H_2O/Al_2O_3		1600 b		1480 s	
NH_3/Al_2O_3			1580 s		1460 s

*R – NH_4ReO_4.

The results obtained in this work lead to the conclusion that the surface rhenium species in the systems 3.3 and 9.9 wt.% NH_4ReO_4/Al_2O_3 do not lead to a generation of strong Lewis type acidic centres. In contrary in the systems 3.3 wt.% NH_4ReO_4/Al_2O_3-SiO_2 and 17.8 wt.% NH_4ReO_4/Al_2O_3 strong Lewis acidic centres are formed. This has been recently proved by Schekler-Nahama *et al.* for the alumina systems [6]. Therefore, it can be assumed that the rhenium species produced in the reaction with the basic groups of aluminium gel do not show the properties of strong Lewis type acids. Such properties, however, characterize the compounds produced in the reaction of rhenium precursor with appropriate acidic -OH groups on the surface of alumina or alumina-silica gels. These compounds, contrary to the former ones reveal high activity in the reactions of olefin metathesis [6,12]. It is reasonable to assume that these two kinds of compounds exhibit a completely different structure. This structural differentiation was postulated for the systems, in which perrhenate was deposited on aluminium gel [1,14] and for those in which it was deposited on alumina-silica gels [1].

Recent studies [6] have shown that during preparation of the systems with alumina gel used as a support, the surface aluminium-rhenium species are formed showing the stoichiometry of aluminium perrhenate. The process involves extraction of aluminium ions from the lattice of the support. Therefore, it can be assumed that a similar process takes place in preparation of the catalysts studied, so that the aluminium ions are extracted by rhenium species from the aluminium and alumina-silica gels. A similar case of the aluminium ions extraction by molybdenum compounds has been recently described in [15,16]. The reaction with basic -OH groups should lead to formation of perrhenate structures, in the case of aluminium gel – to formation of aluminium perrhenate. It has been established that it is possible to obtain this compound in the reaction of Re_2O_7 with aluminium hydroxide [17]. If the reaction runs with participation of the acidic -OH groups, the formation of surface species of the structure of alumina-rhenium garnet in which aluminium cations form strong Lewis type acidic centres has been suggested [1]. The formation of surface rhenium complexes bonded exclusively to aluminium ions of the support surface in the 3%wt Re_2O_7/24.3 wt% Al_2O_3 alumina-silica catalyst, was also recently postulated by Mol [18].

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