THERMAL BEHAVIOUR OF NH₄ReO₄ 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 NH₄ReO₄/Al₂O₃-SiO₂ (25 wt% SiO₂ and NH₄ReO₄/Al₂O₃ containing 1.1, 3.3 and 3.3, 9.9, 17.8 wt% NH₄ReO₄. Thermal decomposition of NH₄ReO₄ on the supports used begins with release of ammonia, which is strongly bound with the surface in the system of 3.3 wt% NH₄ReO₄/Al₂O₃, 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 Al₂O₃-SiO₂ in the amount of 1.1 or 3.3 wt% undergoes partial thermal decomposition to ReO₂ 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 NH₄ReO₄ on Al₂O₃ and Al₂O₃-SiO₂

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: NH₄ReO₄/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 NH₄ReO₄/inorganic gel systems were prepared by pore volume impregnation of the inorganic gel with calculated amounts of an aqueous solution of ammonium perrhenate (MZIPP-Plock), followed by drying overnight at 383 K in air for 16 h. Inorganic gels used as the supports were α-alumina (Ketten CK 300, 80–250 μm) and silica-alumina (Akzo SA-HA, 25 wt% Al₂O₃, 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 cm³ 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% NH₄ReO₄/Al₂O₃–SiO₂ system at various temperatures within the range 373–873 K. The weight percentage of the catalyst was nominal, calculated from