CORRELATION BETWEEN THE REACTIVITY AND THE STRUCTURAL AND THERMAL PROPERTIES OF SUPPORTED METAL NITRATES

S. Békássy¹, T. Cseri¹, G. Kenessey², G. Pokol³, K. Tomor³ and G. Liptay²

¹DEPARTMENT OF ORGANIC CHEMICAL TECHNOLOGY
²DEPARTMENT OF INORGANIC CHEMISTRY
³DEPARTMENT OF GENERAL AND ANALYTICAL CHEMISTRY,
TECHNICAL UNIVERSITY OF BUDAPEST, H-1521 BUDAPEST, HUNGARY

Montmorillonite-supported iron(III) nitrate and copper(II) nitrate reagents, and other supported metal nitrates prepared in the same way, were investigated by thermal and X-ray powder diffraction methods. The metal nitrates are present on the support in the form of crystalline hydrate and not as acetone solvate as supposed earlier. Thermal decomposition of metal nitrates that are active in model reactions proceeds in a different way from that of the practically inactive nitrates. In the former case, water release and nitrate decomposition itself are simultaneous process. These and other results contributed to determination of suitable reaction conditions for the montmorillonite-supported reagents.

Keywords: metal nitrates, montmorillonite-supported reagents

Introduction

The direction and rate of organic reactions can be modified significantly if one of the reactants is deposited on an appropriate (usually inorganic) material, which is itself inactive. In this manner, effects similar to that of catalysts can be achieved: milder reaction conditions may be used under which even sensitive materials can be handled, better or special selectivity can be attained, and reactions can be realized which are not feasible under classical conditions. An additional advantage is that the product can be separated and worked-up easily because of the heterogeneous system. The use of such supported reagents is expanding in organic syntheses [1-3].

Simple and inexpensive representatives of supported reagents are two metal nitrates deposited on the lamellar clay mineral K10 montmorillonite [4]: iron(III) nitrate (named CLAYFEN) and copper(II) nitrate (CLAYCOP) [5, 6]. They are suitable, for instance, for oxidizing alcohols to aldehydes or ketones, oxidative...
coupling of thiols to disulphides, for cleavage of thio- and selenoacetals, Diels-Alder cycloaddition or mononitration of phenols.

In spite of their versatile application there are only few and partly contradictory data in the literature concerning their structure:

- K10 montmorillonite is acidic, this acidity is needed in the chemical reaction, therefore the clay has to be water-free [7];
- the iron(III) nitrate is present in CLAYFEN in water-free form as an unstable acetone solvate; the support is necessary for the stabilization of this solvate, which in itself is explosive [5];
- CLAYCOP prepared under the same conditions contains about 10% of water [6];
- according to DSC studies CLAYFEN decomposes above 59°C with a half-life time of 14 min at 80°C [5].

This investigation was undertaken to study the structure of CLAYFEN and CLAYCOP reagents in order to promote their practical application and to determine suitable reaction conditions. The work has been extended to other supported metal nitrates (Co(II), Cr(III), Mn(II), Ni(II), Zn(II)) prepared in an analogous way in order to generalize the observations.

Experimental

Preparation of the supported metal nitrates [5, 8]

The crystalline metal nitrate hydrate was dissolved in acetone (e.g. 22.5 g Fe(NO₃)₃·9H₂O or the same molar quantity of other metal nitrate in 375 cm³) and the K10 montmorillonite (30 g) was added. After 5–10 min of impregnation under stirring the solvent was carefully removed in a rotating vacuum evaporator at a temperature not exceeding 50°C. The dry precipitate was powdered.

Model reactions [8]

Oxidation: benzyl alcohol to benzaldehyde or 1-phenyl-ethanol to acetophenone (60°C, in n-hexane)

Nitration: 4-hydroxy-benzaldehyde to 4-hydroxy-3-nitro-benzaldehyde (25°–60°C, in toluene)

Thermoanalytical studies

TG-DTG-DTA-MS curves were recorded using a Mettler TA-2 + Balzers MS QMG 311 coupled system. Sample 200 mg in platinum crucible, heating rate 6 deg-min⁻¹, N₂-flow 5 l·h⁻¹, 100 mg α-Al₂O₃ as reference material.

J. Thermal Anal., 40, 1993