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

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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 $Fe(NO_3)_3 \cdot 9H_2O$ or the same molar quantity of other metal nitrate in 375 cm^3) 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}, N$_2$-flow 5 l·h^{-1}, 100 mg α-Al$_2$O$_3$ as reference material.

Thermoemanation studies

Measurements were made using a DuPont 916 TEA instrument. Sample 5 mg, heating rate 8 deg·min^{-1}, N$_2$-flow 1.8l·h^{-1}

X-ray powder diffraction studies

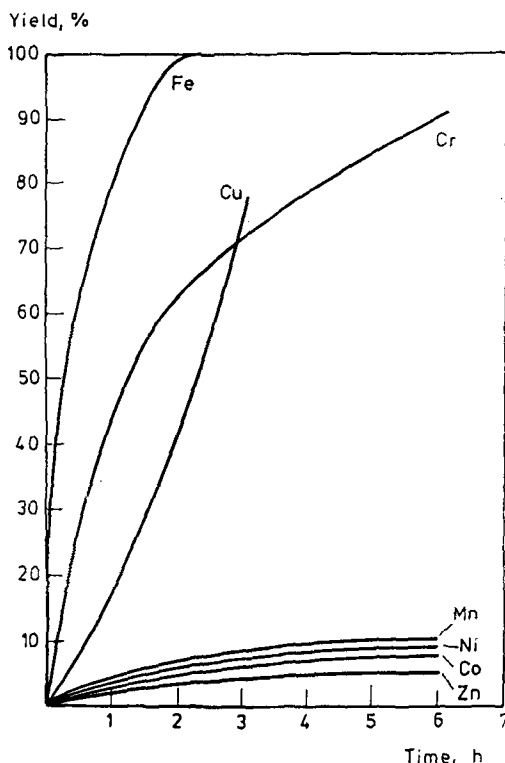Diffraction patterns were recorded on an HZG-4C type diffractometer. Conditions: CoK$_\alpha$ radiation, Fe filter, scan rate 1°θ·min^{-1}.

Fig. 1 Reactivity of supported metal nitrates in oxidation of benzyl alcohol

Results and discussion

In addition to CLAYFEN and CLAYCOP, chromium(III) nitrate supported on K10 montmorillonite was found to be active in the model reactions (referred to as CLAYCHROM). The other metal nitrates gave only very low yield even after

long reaction times. Data on the oxidation of benzyl alcohol are presented in Fig. 1.

Results of the thermoemanation investigations contradict literature data [5]: organic material could be detected neither in CLAYFEN nor in CLAYCOP. These reagents do not contain even traces of acetone and thus the metal nitrate is not present as acetone solvate. The same negative results were obtained for the other supported metal nitrates, independent of their activity.
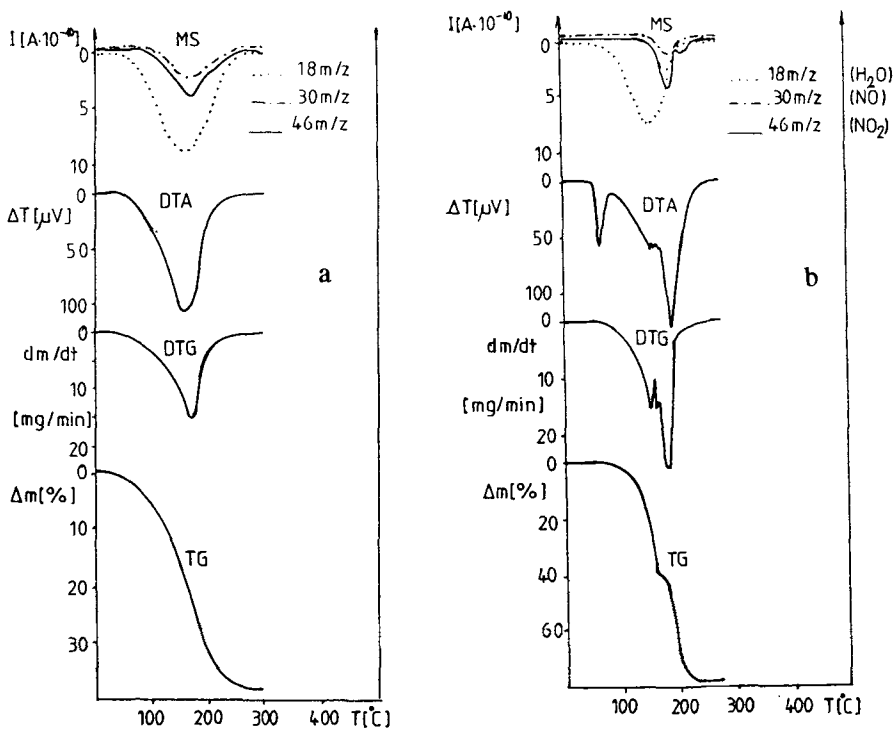

Fig. 2 Thermoanalytical curves of a./ CLAYFEN and b./ Fe(NO₃)₃·9H₂O

Thermogravimetric TG) curves of CLAYFEN and CLAYCOP can be explained only if the total amount of crystallization water of the metal nitrates is present in the reagents. Thermoanalytical curves of CLAYFEN are shown in Fig. 2/a. Similar results were obtained for the other supported metal nitrates, regardless of whether they were active in model reactions (Fig. 3/a CLAYCHROM) or not.

According to the X-ray diffraction patterns the salts are, at least partly, crystalline on the support, and the water is present as water of crystallization of the nitrate. The diffraction lines are sharp and intense (*e.g.* CLAYCOP, Fig. 5) and K10 supported zinc(II)nitrate and coincide with the lines of the pure salts. For

CLAYFEN (Fig. 6) the lines also coincide, but are less intense. The iron(III) nitrate is present on the support mostly in X-ray amorphous form, in accordance with the fact that the salt does not dissolve readily in acetone during preparation of the reagent but forms a fine suspension.
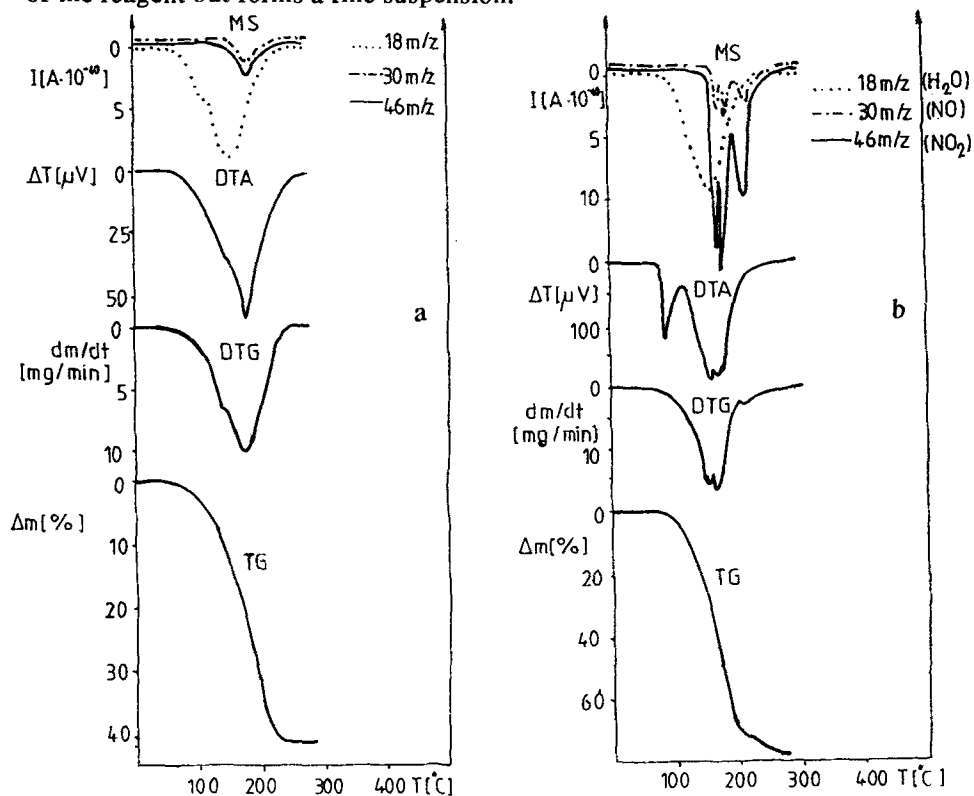

Fig. 3 Thermoanalytical curves of a./ CLAYCHROM and b./ $Cr(NO_3)_3 \cdot 9H_2O$

TG-MS measurements enabled water loss and nitrate decomposition to be distinguished. Based on the course of the decomposition the investigated nitrates can be classified into two groups:

a./ For nitrates which were active in the model reactions, water release was accompanied by decomposition of the nitrate, the latter process beginning at least at the temperature of maximum rate of water loss (Figs 2/b and 3/b), *i.e.* nitrate decomposition takes place simultaneously with water release and the intermediate may be active. These decomposition characteristics are confirmed also by literature data [9, 10],

b./ For practically inactive nitrates, the decomposition of the nitrate occurs as a separate process after water release is complete (*e.g.* decomposition of zinc(II)

nitrate in Fig. 4); thus a dehydrated metal nitrate can be obtained as an inter-mediate of the thermal decomposition, in good agreement with earlier results [10].
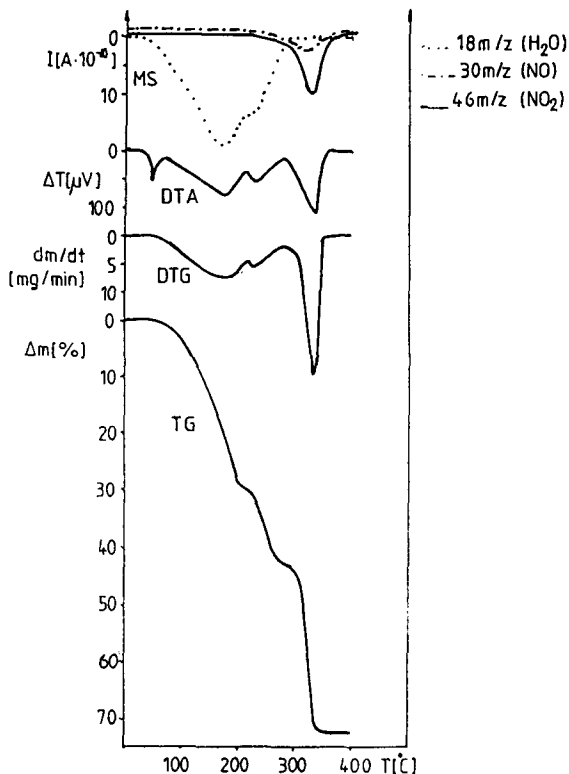

Fig. 4 Thermoanalytical curves of $Zn(NO_3)_2 \cdot 6H_2O$

Two differences were observed between the decomposition of the pure salts and supported ones (Figs 2 and 3):

a./ the start of decomposition generally shifts towards lower temperatures for the supported nitrates,

b./ some partial decomposition processes merge due to the influence of the support.

As decomposition of the supported nitrates begins in some cases at 30°–40°C (*e.g.* CLAYFEN, on Fig. 2), decomposition can occur during preparation. Thus the evaporation step has to be performed very carefully, *e.g.* at max. 35°C instead of 50°C proposed in the literature [5].

The thermoanalytical curves and decomposition temperatures derived from them can help to determine the temperature limit of application of the reagents
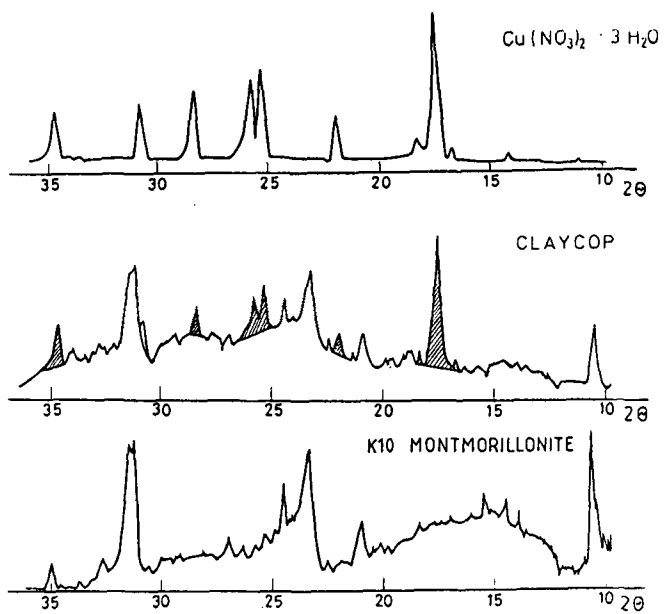
Fig. 5 Comparison of the X-ray diffraction patterns of CLAYCOP and Cu(NO3)2·3H2O
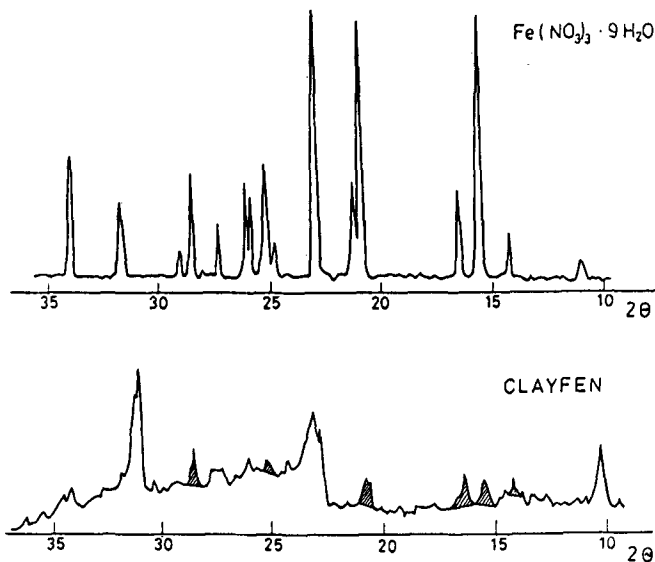
Fig. 6 Comparison of the X-ray diffraction patterns of CLAYFEN and Fe(NO3)3·9H2O

where the decomposition rate of the metal nitrate is lower than the rate of the reaction. Thus for CLAYFEN:

– mononitration of 4-hydroxy-benzaldehyde can be completed at 60°C within 2–3 h with the same good yield and selectivity [8], instead of the 70 h mentioned in the literature [5],

– phenol ethers which are less activated than phenols, *e.g.* anisole, can also be nitrated.

These experiences and results contribute to the realization of different reactions. Investigations are continuing, among others with further metal nitrates.

References

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Zusammenfassung — Mittels thermischen und Debye-Scherrer-Methoden wurden montmorillonitgetragene Eisen(III)nitrat- und Kupfer(II)nitratreagenzien sowie andere, auf die gleiche Weise dargestellte getragene Metallnitrate untersucht. Die Metallnitrate sind auf dem Träger in Form von kristallinen Hydraten und nicht wie früher angenommen in Form von Aceton-Solvaten vorhanden. Die thermische Zersetzung von in Modellreaktionen aktiven Metallnitraten verläuft anders als die thermische Zersetzung der praktisch inaktiven Nitrate. Im ersteren Falle verlaufen die Freisetzung von Wasser und die Nitratzersetzung selbst simultan ab. Diese und andere Ergebnisse trugen zur Bestimmung geeigneter Reaktionsbedingungen für montmorillonitgetragene Reagenzien bei.