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Characterization of metal nitrates and clay supported metal nitrates by thermal analysis

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Abstract

Hydrated metal nitrates of Zn, Mn, Ni, Co, Cu, Fe, Cr and Bi, either pure or supported by an acid treated montmorillonite (K10 from Süd-Chemie), were studied using X-Ray diffraction, TG, DTG, DTA, together with MS analysis of gaseous products formed during thermal decomposition. The decomposition products were also analysed by thermoemanation analysis. The metal nitrates were present on the support in the form of crystalline hydrates and not as acetone solvates as supposed earlier. The thermal decomposition of supported metal nitrates started at lower temperatures than those observed for bulk metal nitrates. The supported reagents were tested in different organic oxidation and nitration model reactions. The activities in organic chemical reactions were controlled by the thermal stability of the supported metal nitrates, as expected for reactions involving nitrogen oxides as active intermediates. The suitable reaction conditions were obtained from thermal analysis.

Keywords: Metal nitrates; Montmorillonite; Supported reagents; Thermal stability; TG-DTG-DTA-MS; Selective oxidation

1. Introduction

The direction and the rate of organic reactions can be modified significantly if one of the reactants is deposited on an appropriate material, which is itself usually inactive.

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Chemists have used highly dispersed mineral solids, with extensive specific areas, for a long time. The last few years have seen a considerable extension of the supported reagent technique. These novel reagents have advantages over the conventional homogeneous solution techniques including, i) milder reaction conditions may be used under which even fragile materials can be handled, ii) better or special selectivities can be obtained, and iii) greater ease of set-up and of work-up because of the heterogeneous system, which facilitates the separation of products. The variety and the use of these supported reagents are expanding [1–4].

The group of Laszlo has successfully investigated two of these reagents: iron(III) nitrate supported on K10 montmorillonite (named CLAYFEN) and copper(II) nitrate supported on K10 (named CLAYCOP). These materials were applied to several organic reactions, such as cycloaddition of the Diels-Alder type [5–7], porphyrin synthesis by condensation of pyrrole with aldehydes [8], oxidation of alcohols to aldehydes or ketones [9,10], benzoins to benzils [11], oxidative coupling of thiols to disulfides [12], conversion of alcohols to nitrites [10] and of thiols to thionitrites [12], acetal formation from alcohols [13], hydrolytic cleavage of thioacetals and selenoacetals [14], conversion of various imino derivatives to carbonyl compounds [15,16], preparation of azides from hydrazines [17], aromatization of dihydropyridines [18], or introduction of functional groups into molecules such as nitration of phenols [19,20].

In spite of their versatile applications data describing the structure of these clay supported metal nitrates are scarce and partly contradictory. Iron (III) nitrate was proposed in CLAYFEN to be an anhydrous species, namely an unstable acetone solvate where the support is necessary for the stabilization of the solvate, which in itself is explosive [21]. Left in air contact at room temperature, CLAYFEN retains its activity for only a few hours [9]. It may be stored for a few days and retains its activity when it is covered with pentane immediately after preparation; the hydrocarbon is evaporated prior to use. It was proposed as good practice to use only freshly prepared reagents since about 40% of the reactivity was lost upon standing exposed to air for 4 h, or under pentane for 24 h. The thermal stability of CLAYFEN has been investigated [21] by differential scanning calorimetry. Above 59°C, it decomposed with an enthalpy release of 83.7 J/g. This was a first order process, with calculated half-lives of 53 min at 69°C (the temperature of boiling hexane) or of 14 min at 80°C (in boiling benzene). The group of Laszlo also investigated the reactivity of the acetone solvate of iron(III) nitrate obtained by concentration under vacuum of an acetone solution of iron(III) nitrate nonahydrate. This solvate was a highly unstable oil with a deep red color. The analysis performed before its decomposition showed the presence of a substantial amount of organic material, responsible for a 10% carbon content. The IR spectrum of this oil has bands at 1220 and 1630 cm^{-1}, assigned to a bidentate nitrate group on iron(III) [20]. Their working hypothesis was that this oil contained $Fe(NO_3)_3{*}2(CH_3)_2CO$. In this supported system, K10 montmorillonite carried an acid function, needed in the chemical reaction, therefore the clay had to be water-free [22].

CLAYCOP was prepared under the same conditions as CLAYFEN. It was concluded that CLAYCOP contained about 10% of water [23]. CLAYCOP reagent, also based on a salt forming covalent bidentate complexes upon dehydration [20,21], showed no loss of reactivity in the applications described hereafter, even after standing in an open powder box for one month.

Since the decomposition of the metal nitrates is needed to produce the active agent (NO^+) accepted as intermediate for the oxidation of alcohols [9,10] and nitration of phenols [19,20], one of the best methods of investigation in this respect is thermal analysis. We have recently published some of our results [24,25].

This study examines eight metal nitrates [Mn(II), Co(II), Ni(II), Zn(II), Cu(II), Cr(III), Fe(III), Bi(III)] supported on clays. The main reasons of their choice are: i) these metal nitrates are abundant and cheap, and ii) the decomposition of metal nitrates should be related to the stability of the nitrate ligand.

The aim of the present work was therefore to prepare these different clay supported metal nitrate reagents, to investigate their thermal properties and stabilities in detail, to describe the thermal decomposition of metal nitrates, to compare the thermal properties of non supported and supported metal nitrates, and finally to check their chemical activities in different oxidation and nitration model reactions.

2. Experimental

2.1. Preparation of the supported metal nitrates

The preparation of these supported reagents has been described several times [9,22,25]. In brief, the required amount of hydrated metal nitrate was added to acetone (187.5 ml) in a 0.5 litre evaporating flask. The mixture was stirred vigorously for 15 min until complete dissolution of the crystals of the nitrate (in the case of iron, chromium and bismuth nitrates suspensions were observed). K10 clay (15 g) was added in small amounts and stirring was continued for another 15 min. The solvent was then removed from the resulting suspension under reduced pressure (rotary evaporator) on a water bath below 50°C. After the first step of drying, the dry solid crust adhering to the walls of the flask was flaked off and crushed with a spatula, and rotary evaporator drying was continued. The dry precipitate was powdered, the procedure yielded a floury powder.

K10 clay is an industrial product and is manufactured by the high temperature acidic treatment of a Bavarian bentonite, it was purchased from Süd-Chemie, München.

For the preparation of different supported reagents (Table 1) the nitrate / support ratio was constant: 10 mmol nitrate(ion)/ 1.8 g support.

2.2. Thermoanalytical studies

TG-DTG-DTA curves were recorded using a MOM OD-2 Derivatograph. The sample (200 mg) was charged in a platinum crucible. The heating rate was 5°C/min for the metal nitrates either pure or supported, and 10°C/min for the support in air atmosphere.

TG-DTG-DTA-MS curves were recorded using a Mettler TA-2 coupled with a Balzers MS QMD 311 mass spectrometer. The sample (200 mg) was also charged in

Table 1
Amounts of metal nitrates used for 15 g K10 and 187,5 ml acetone, in the preparation of supported reagents

Supported reagent	Metal nitrate	Amount of metal nitrate
CLAYFEN	$Fe(NO_3)_3{*}9H_2O$	11.25 g
CLAYCOP	$Cu(NO_3)_2{*}3H_2O$	10.00 g
CLAYCHROM	$Cr(NO_3)_3{*}9H_2O$	11.10 g
CLAYBIS	$Bi(NO_3)_3{*}5H_2O$	12.70 g
CLAYZIN	$Zn(NO_3)_2{*}6H_2O$	12.40 g
CLAYCOB	$Co(NO_3)_2{*}6H_2O$	12.15 g
CLAYMAN	$Mn(NO_3)_2{*}4H_2O$	10.50 g
CLAYNIC	$Ni(NO_3)_2{*}6H_2O$	11.12 g

a platinum crucible. The heating rate was 6°C/min; the N_2 flow was 5 l/h. The reference material (100 mg) was α-Al_2O_3.

2.3. Thermoemanation studies

The measurements were made using a DuPont 916 TEA instrument. The weight of sample was 5 mg, the heating rate was 8°C/min, and the N_2 flow rate was 1.8 l/h. The analysis of gaseous products was carried out by FID detection.

2.4. X-Ray diffraction measurements

X-Ray powder diffraction patterns were recorded on a HZG-4C type diffractometer, using Cu K_α radiation ($\lambda = 1.79$Å), Fe filtered, using a scan rate of 1°/min.

2.5. Model reactions used

1) Oxidation of benzyl alcohol to benzaldehyde. Typical reaction conditions were: benzyl alcohol 10 mmol, CLAYFEN 3.14 g corresponding to a molar ratio NO_3^-/alcohol = 1/1, solvent n-hexane or n-heptane (50 ml). The temperature was varied in the range of 30–90°C. The reactions were monitored by GC.

2) Nitration of 4-hydroxy-benzaldehyde to 3-nitro-4-hydroxy-benzaldehyde. Typical reaction conditions for CLAYFEN were: 4-hydroxy-benzaldehyde 10 mmol, in 50 ml of toluene as solvent, molar ratio NO_3^-/substrate = 1.0 to 1.6.

3. Results

3.1. Characterization

X-Ray diffraction

The X-ray powder diffraction pattern of CLAYCOB is compared to the spectra of K10 and bulk cobalt(III) nitrate in Fig. 1, and the same comparison is reported in Fig. 2

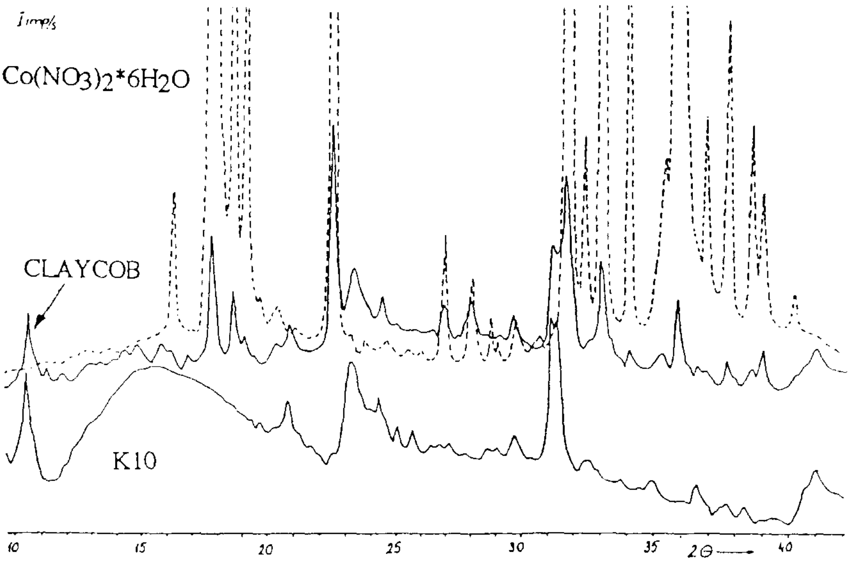

Fig. 1. XRD powder diffraction patterns of CLAYCOB, K10 and cobalt(II) nitrate.

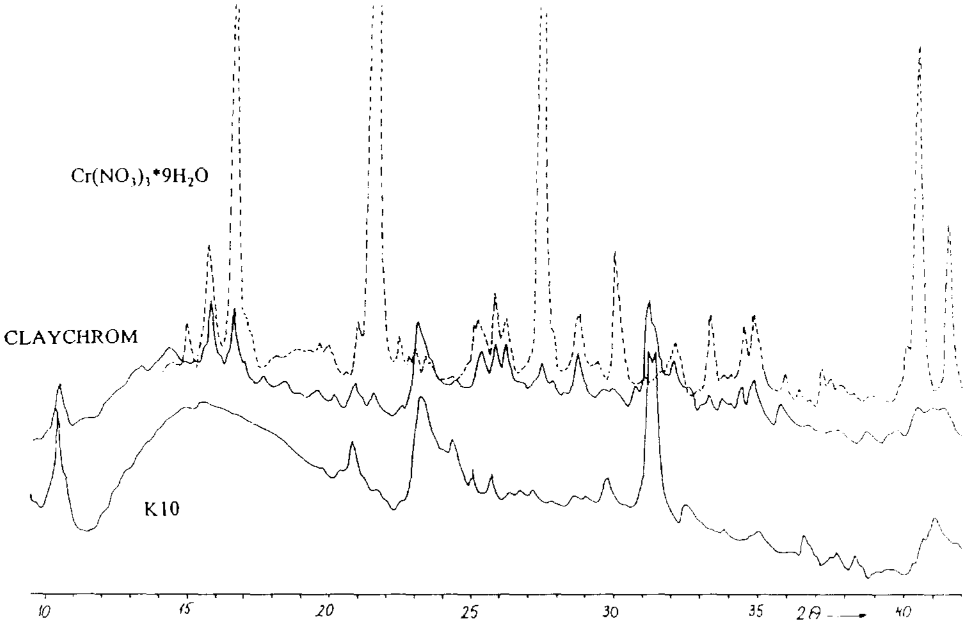

Fig. 2. XRD powder diffraction patterns of CLAYCHROM, K10 and chrom(III) nitrate.

for the Cr(III) nitrate. The XRD spectra of CLAYFEN and CLAYCOP have been reported previously [24]. All these spectra show the same behaviour. The supported reagent exhibited the XRD lines characteristic of the hydrated compound. The intensity was low, and the lines were broader compared to the pure compound, which suggests that the supported nitrate was in the form of small crystals, or partly amorphous. The crystallinity of the supported nitrate was controlled by the solubility of the starting salt in acetone. The nitrates (Bi(III), Fe(III), Cr(III)) which are hardly soluble in acetone, then gave highly saturated solutions, were amorphous when supported on the clay, in agreement with the classical laws of crystal growth. The nitrates which are soluble in acetone (Cu(II), Ni(II), Zn(II), Co(II)) yielded bigger crystals on the support.

Thermal analysis

The results obtained from the thermal analyses are exemplified in Figs. 3 and 4 for the decomposition of pure cobalt(II) and copper(II) nitrates . The comparison of pure and supported nitrates is reported in Figs. 5, 6 for Bi(III) and Cr(III). From these curves several determinations can be made. These are the melting point of the nitrate, weight loss, temperatures of the different decomposition steps, and the nature of the gases evolved in the decomposition.

It is well known from the literature that bulk nitrates can decompose with or without concomitant dehydration [26]. In the case of cobalt(III) nitrate for instance (Fig. 3), the loss of water occurs as a first step, and the decomposition yielding NO_x in a second step, at higher temperature. In the case of Cu(II), Bi(III), Cr(III) (Figs. 4–6) and Fe(III) nitrates [24] dehydration and decomposition were not separated. Water release was accompanied by the decomposition of the metal nitrate.

In the case of the pure nitrates, the weight loss corresponded to the conversion to the oxide. In the case of supported nitrates, the weight loss will depend on the solvation of the nitrate either as an anhydrous solvate of acetone, or a hydrate. The weight losses measured for the supported nitrates are reported in Table 2 and compared to the calculated theoretical losses corresponding to the decomposition of the hydrated nitrate, contained in the clay, to the anhydrous oxide, taking into account also the weight loss of clay dehydration up to 400°C.

The measured and calculated results are practically identical, especially in the case of chromium(III), iron(III), copper(II) and bismuth(III) nitrates. These thermogravimetric results of the supported materials show that all the crystallization water of the nitrates was retained in the supported reagents. The results also suggest that the mechanism proposed for the decomposition of bulk metal nitrates is valid for those supported on the clay as well.

Most metal nitrates melt at a lower temperature after deposition on the support as reported in Table 3. In particular, the amorphous nitrates (Cr(III), Fe(III), Cu(II), Bi(III)) and Co(II) nitrate started to decompose at lower temperatures than the pure metal nitrates. This shift was expected from the thermodynamic properties of small crystals.

The deposition of metal nitrates on the support also reduced the temperature at which the decomposition started as reported in Table 3. The temperature at which this decomposition is completed was similarly reduced (Table 4).

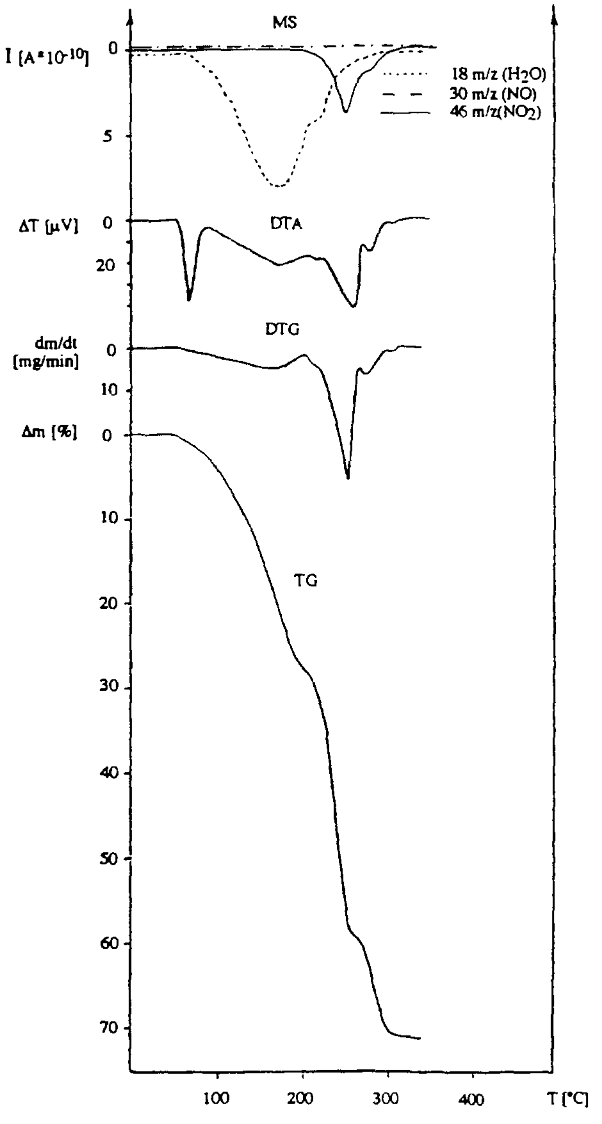

Fig. 3. Thermoanalytical curves of $Co(NO_3)_2{*}6H_2O$.

Another characteristic of the thermal behaviour of supported nitrates was that some decomposition steps, observed in the case of the pure nitrates, disappeared or were not separated for the supported material (Table 5). As reported above, Bi(III), Fe(III) and Cr(III) nitrates did not dissolve in acetone but formed fine suspensions. Using XRD, these nitrates appear as particles of very small size when supported. In these cases, a larger difference was observed between the temperature of decomposition of the pure

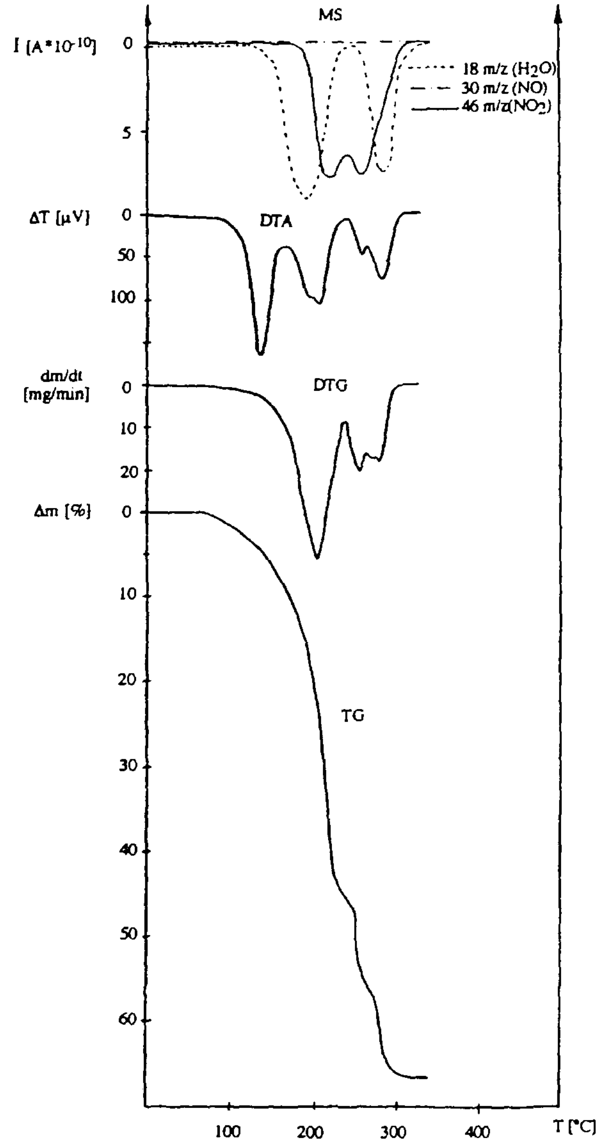

Fig. 4. Thermoanalytical curves of $Cu(NO_3)_2{*}3H_2O$.

nitrate and that of the supported one (Tables 4 and 5). For the other nitrates which appeared more crystalline when supported on the clay, this difference was less important. This shift may then be ascribed in part to the amourphous state of the supported nitrate. However, the observation of a lower temperature of decomposition in the case of the crystalline nitrates suggests that the acidity of support can also play a role, probably by the possible hydrolysis of the metal nitrate.

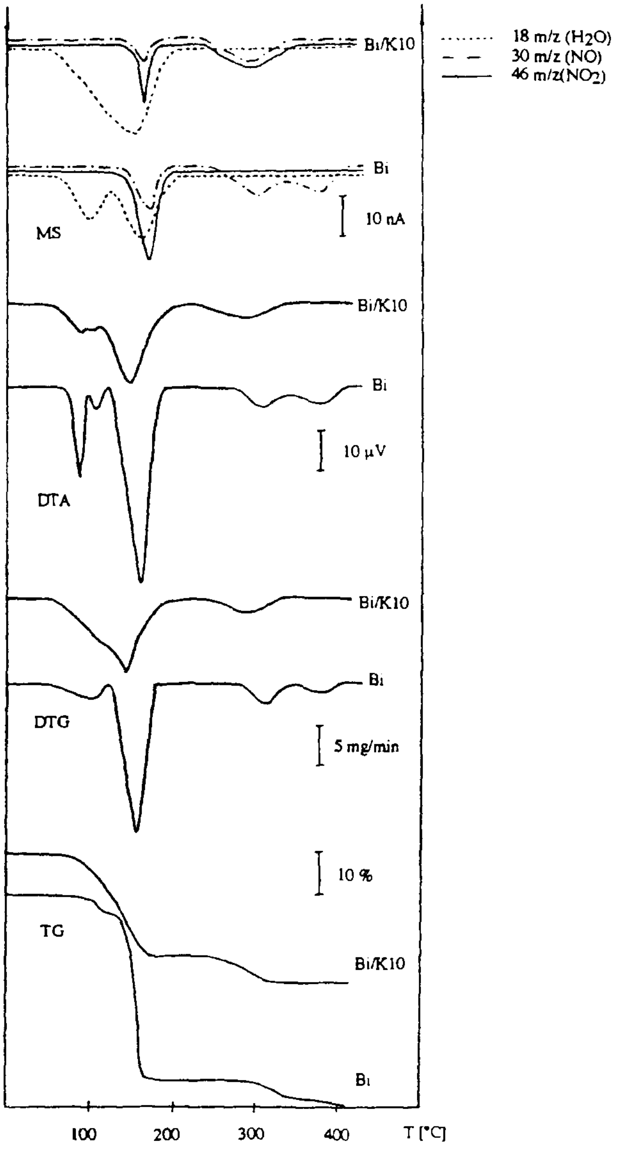

Fig. 5. Thermoanalytical curves of CLAYBIS (Bi/K10) and Bi(NO$_3$)$_3$*5H$_2$O.

Thermoemanation studies

The aim of this investigation was to check the possible existence of acetone solvates. The gaseous products of decomposition of all supported reagents (Fe(III), Cu(II), Bi(III), Cr(III), Mn(II), Ni(II), Zn(II) and Co(II) nitrates supported on K10) were analyzed with FID detection. From these thermoemanation investigations, no organic

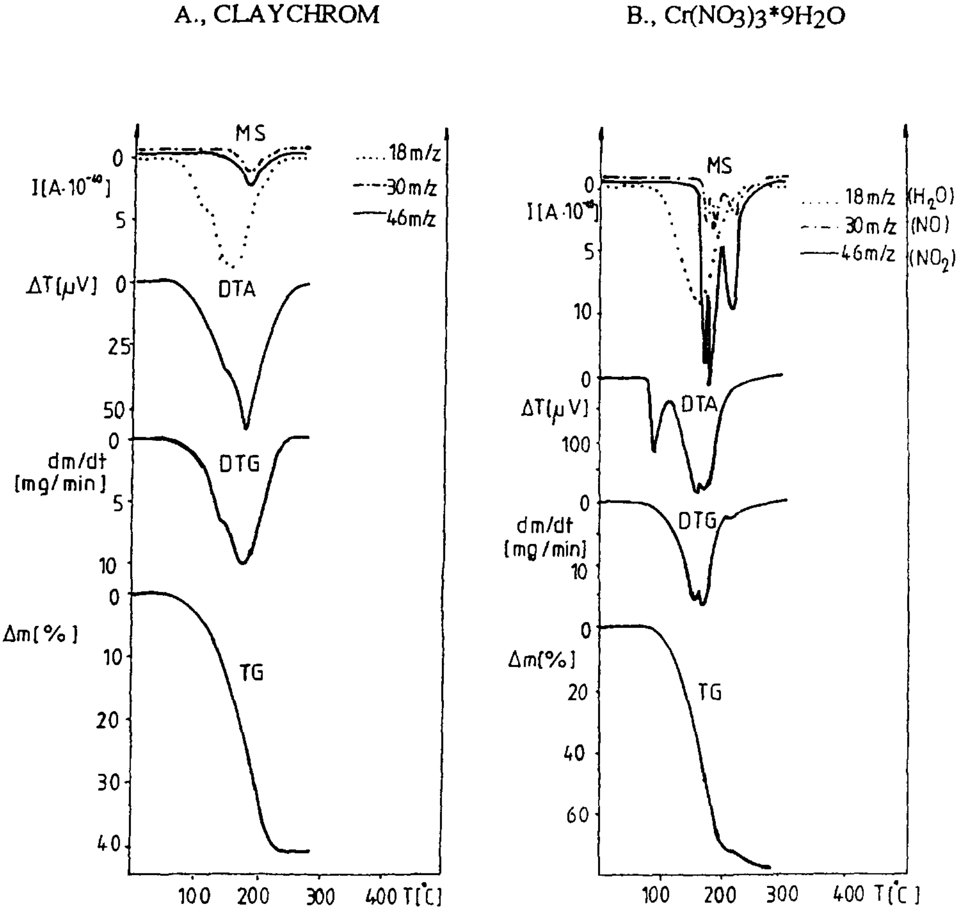

Fig. 6. Thermoanalytical curves of a) CLAYCHROM and b) $Cr(NO_3)_3{*}9H_2O$.

material was detected on any of the supported metal nitrates. Thus, these reagents did not contain even traces of acetone.

3.2. *Model reactions*

It was recently reported [24], that the order of reactivity of the different supported metal nitrates was practically independent of the model reaction, and similar patterns were obtained for the oxidation of benzyl alcohol or nitration of substituted phenols, i.e.,

$$\mathrm{Bi(III)} > \mathrm{Fe(III)} > \mathrm{Cr(III)} > \mathrm{Cu(II)} >\!>\!> \mathrm{Mn(II)} \geq \mathrm{Ni(II)} \geq \mathrm{Co(II)} \geq \mathrm{Zn(II)}$$

The observation of the same patterns suggests that the same active intermediate is involved and NO^+ was formerly proposed. Since the decomposition of the nitrates

Table 2
Comparison of measured total weight loss and the calculated one related to the amount of hydrated nitrate used for the preparation of the supported reagents. (The analyses were carried out in air and the decompositions were followed up to 400°C.)

Starting material	Residual material	Weight loss%	
		Calculated	Measured
$Zn(NO_3)_2{*}6H_2O/K10$	$ZnO/K10$	38.3	41.0
$Mn(NO_3)_2{*}4H_2O/K10$	$MnO_2/K10$	35.3	32.8
$Ni(NO_3)_2{*}6H_2O/K10$	$NiO/K10$	38.7	35.0
$Co(NO_3)_2{*}6H_2O/K10$	$Co_3O_4/K10$	37.9	39.0
$Cr(NO_3)_3{*}9H_2O/K10$	$Cr_2O_3/K10$	39.9	40.0
$Fe(NO_3)_3{*}9H_2O/K10$	$Fe_2O_3/K10$	40.1	40.0
$Cu(NO_3)_2{*}3H_2O/K10$	$CuO/K10$	33.0	33.0
$Bi(NO_3)_3{*}5H_2O/K10$	$Bi_2O_3/K10$	31.3	31.0

Table 3
Melting points and temperatures of beginning of decomposition measured for the different metal nitrates and supported reagents

Metal nitrate	Melting point (°C)		Starting temperature of decomposition (°C)	
	pure salt	supported	pure salt	supported
Zn	36	not detected	50	50
Mn	30	not detected	40	40
Ni	50	55	50	50
Co	55	40	50	40
Cr	67	not detected	60	50
Fe	49	30–35	60	35–40
Cu	116	105	90	50
Bi	75	60–65	50	30

Table 4
Temperatures (°C) of the end of the thermal decomposition of metal nitrates

Nitrate compound	Not supported	Supported	Difference (supported - not supported)
Zn	310	280	−30
Mn	200	195	−5
Ni	320	290	−30
Co	270	230	−40
Cr	290	190	−100
Fe	270	200	−70
Cu	270	280	+10
Bi	370	265	−105

Table 5

Temperatures (°C) of the maximal rates of formation of different gaseous decomposition products obtained from TG-MS coupling. (The nitrates of Mn and Ni, as well as the supported reagents of Zn, Ni, Mn and Co were not mesured by TG-MS.)

	H_2O	NO_2	NO
$Zn(NO_3)_2*6H_2O$	165	–	–
	(230)	–	–
		320	320
$Co(NO_3)_2*6H_2O$ (Fig. 3)	175	–	–
	235	–	–
	–	255	–
$Cu(NO_3)_2*3H_2O$ (Fig. 4)	200	–	–
	–	235	–
	–	270	–
	300	–	–
Cu/K10	130	–	–
	–	–	170
	–	–	220
	–	–	250
$Fe(NO_3)_3*9H_2O$	170	185	185
	–	220	(220)
Fe/K10	170	185	185
$Cr(NO_3)_3*9H_2O$ (Fig. 6)	170	–	–
	–	180	180
	–	195	195
	–	220	220
Cr/K10 (Fig. 6)	170	–	–
	170	195	195
$Bi(NO_3)_3*5H_2O$ (Fig. 5)	110	–	–
	170	185	185
	–	–	305
	–	–	380
Bi/K10 (Fig. 5)	140	180	180
	–	290	290

starts at different temperatures according to the metal used, the reaction temperature should be adapted to each particular case, and the influence of this reaction condition was investigated in the case of the Fe(III), Bi(III) and Cu(II) supported reagents.

a) Oxidation of benzyl alcohol: In all the cases the reactions were 100% selective for benzaldehyde, without overoxidation because no benzoic acid was detected by TLC or HPLC. The results concerning the oxidation of benzyl alcohol by CLAYFEN at 44°C or at 60°C are reported in Fig. 7.

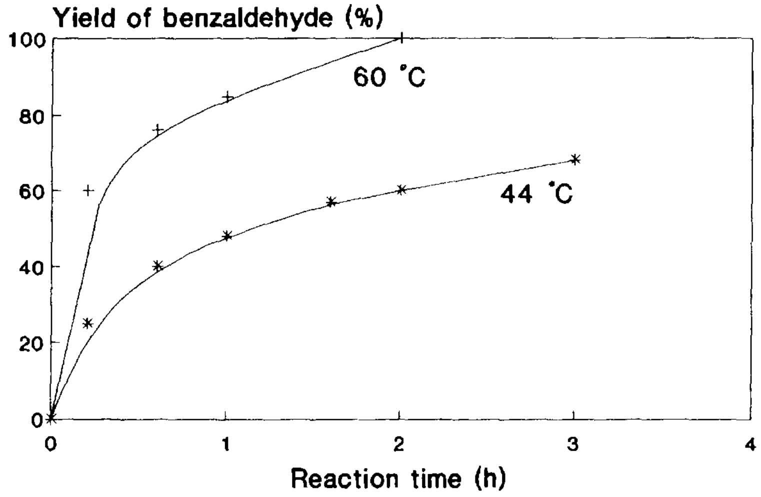

Fig. 7. Oxidation of benzyl alcohol with CLAYFEN. Effect of the reaction temperature. (Reaction conditions: solvent hexane, benzyl alcohol 10 mmol, CLAYFEN 3.14 g, molar ratio NO_3^-/alcohol = 1/1).

From these kinetic curves, the initial rates determined at low conversion are:

$v_0(44°C) = 3.8 \times 10^{-3}$ mol/g*h

$v_0(60°C) = 15.2 \times 10^{-3}$ mol/g*h

Iron(III) nitrate starts to decompose at 35–40°C, and high reaction rates are observed in the same range of temperature. In the two cases we have observed the complete conversion of benzyl alcohol to benzaldehyde, which necessites 5h at 44°C. An increase of temperature has two effects. The rate of the chemical reaction is increased and the rate of decomposition of the nitrate which produces the active agent for the oxidation or nitration is equally increased. If the decomposition is faster than the chemical reaction, the evolution of gaseous nitrous oxide was observed, then a loss of part of the active agent and smaller chemical yields.

From thermal analysis copper(II) nitrate appears more stable than iron(III) nitrate (Table 3). The reaction by CLAYCOP was then carried out at higher temperatures (Table 6).

Table 6
Effect of the reaction temperature on the yield of oxidation of benzyl alcohol to benzaldehyde. Reaction conditions: reaction time 3h, benzyl alcohol 10 mmol, CLAYCOP 3.03 g, molar ratio: NO_3^- / alcohol = 1/1

Temperature of reaction (°C)	Solvent	Yield of benzaldehyde (%)
44	hexane	5
60	hexane	70
75	heptane	94
90	heptane	100

The kinetic curves of the oxidation of benzyl alcohol by CLAYCOP at three different temperatures are reported in Fig. 8. The temperature effect is very important in this case. At 44°C a very slow reaction was observed, in agreement with the fact that the decomposition of the nitrate had not started at this temperature. At higher temperature high chemical yields were observed, which correspond to faster decomposition as well as faster oxidation rates. For instance at 75°C, the reaction was fast and the optimal temperature of application of CLAYCOP as supported reagent may be found in this zone. At this temperature a fast chemical reaction, without appearence of nitrous fumes, was observed. This observation supports the proposal that the chemical reaction follows the decomposition of the nitrate.

From these curves the initial rates can be determined as:

$v_0(44°C) = 4 \times 10^{-5}$ mol/g*h

$v_0(60°C) = 2.5 \times 10^{-4}$ mol/g*h

$v_0(75°C) = 3 \times 10^{-3}$ mol/g*h

The influence of the reaction temperature on the oxidation of benzyl alcohol by the supported bismuth(III) nitrate is presented on Fig. 9. The initial rates determined from these curves are:

$v_0(30°C) = 1.5 \times 10^{-4}$ mol/g*h

$v_0(40°C) = 5.1 \times 10^{-4}$ mol/g*h

$v_0(60°C) = 1.35 \times 10^{-2}$ mol/g*h

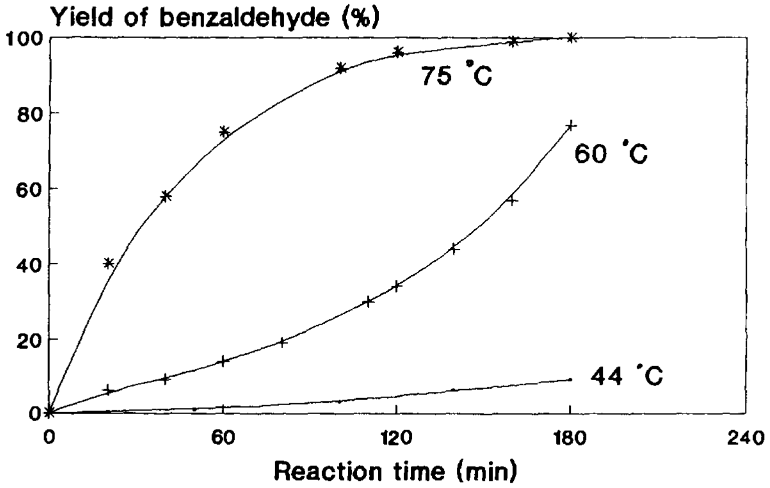

Fig. 8. Oxidation of benzyl alcohol with CLAYCOP. Effect of the reaction temperature. (Reaction conditions: benzyl alcohol 10 mmol, CLAYCOP 3.03 g, molar ratio NO_3^-/alcohol = 1/1, solvent hexane for 44 and 60°C, heptane for 75°C).

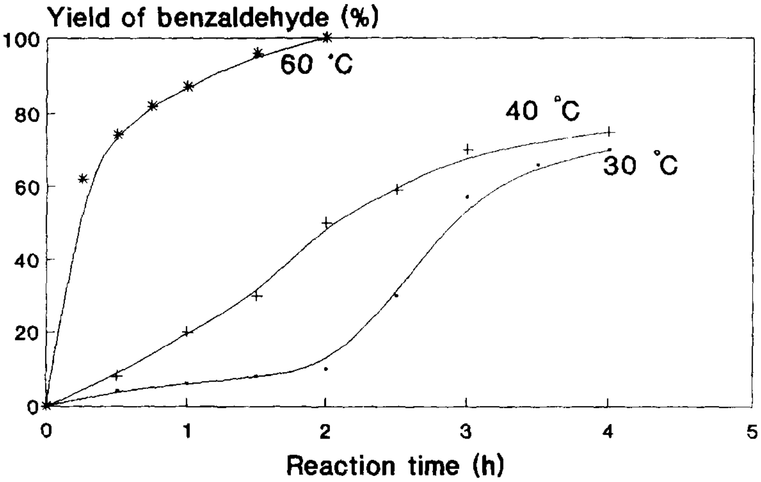

Fig. 9. Oxidation of benzyl alcohol to benzaldehyde with CLAYBIS at different temperatures. (Reaction conditions: solvent hexane, benzyl alcohol 10 mmol, CLAYBIS 3.31 g, molar ratio NO_3^-/alcohol = 1/1).

At low temperature, an induction periode was observed. However, the reaction was fast in agreement with the easy decomposition of bismuth(III) nitrate. At 60°C the reaction rate was very high, and the increase from 40°C to 60°C shows clearly the double effect of temperature.

b) Nitration of substituted phenols: The influence of temperature is expected to be similar in the case of nitration: some of the results obtained on the nitration of 4-hydroxy-benzaldehyde to 3-nitro-4-hydroxy-benzaldehyde by CLAYFEN are reported in Table 7.

A molar ratio of NO_3^-/ substrate = 1.00 did not give a total conversion, and the reaction was slow, particularly at room temperature. The increase of the molar ratio of

Table 7
Study of the effect of the reaction temperature and molar ratio of reactants on the nitration of 4-hydroxy-benzaldehyde to 3-nitro-4-hydroxy-benzaldehyde by CLAYFEN. Reaction conditions: 4-hydroxy-benzaldehyde 10 mmol, solvent toluene. The conversion is measured for 4-hydroxy-benzaldehyde

Reaction time (h)	Temperature of reaction (°C)	Molar ratio NO_3^-/substrate	Conversion (%)	Yield (%) (isolated)
90	room temp.	1.00	86	80
43	60	1.00	87	80
3	60	1.30	100	96
10	110	1.30	80	75
2	60	1.60	100	95

NO_3^-/substrate at 60°C improved the yield. The reaction time can be reduced to 2–3 h, and remarkable chemical yields can be reached with conversions of 100%. A smaller conversion was however observed at 110°C. This can be ascribed to a too fast decomposition of the nitrate at this temperature compared to the rate of the chemical reaction. Similar results have been observed for the nitration of 4-chloro-phenol to 2-nitro-4-chloro-phenol. These results illustrate the importance of the applied temperature for these supported reagents.

4. Discussion

The XRD patterns of some supported nitrates such as CLAYCOP [24] or CLAYZIN, show sharp and intense lines in good agreement with the patterns of the pure salts. In that case, there is a clear direct evidence that the salts are present on the support as crystalline hydrated nitrates. In the case of CLAYFEN, CLAYBIS and CLAYCHROM the position of the XRD lines also agree with the presence of a hydrated nitrate, but their intensity is much lower. These nitrates form super saturated suspensions during the preparation, and their lower crystallinity can be ascribed to the formation of very small crystals.

The thermogravimetric analysis of the clay supported metal nitrates provides evidence that, in all cases, the whole amount of crystallization water of the nitrates is present in the reagents (Table 2). No organic material was detected on any supported reagent by thermoemanation. Thus these reagents did not contain acetone. The metal nitrates were present on the support not as acetone solvate, but as crystalline hydrates. The same results were found by IR spectroscopic investigations [27]. Acetone solvates of metal nitrates proposed by Laszlo [20,22] are probably impossible to form here because the boiling point of acetone is much lower than of water, and their mixture can not give an azeotrope. Therefore the water contained in the original metal nitrates cannot be eliminated during the preparation of the supported reagents.

The formation of hydrated nitrates is also in agreement with the basic ideas of coordination chemistry. Indeed the affinity of water molecules to metallic cations is stronger than the affinity of acetone molecules, or nitrate anions. The decreasing order in the nefelauxetic series is the following [28]:

$$H_2O > NO_3^- > CH_3COCH_3$$

Coordination chemistry then predicts that the inner coordination sphere of the metal will be occupied by water molecules.

The reactivity of these supported reagents has then to be analyzed in terms of stability of hydrated salts, which produce nitrogen oxides in their decomposition. As would be predicted from the results of thermal analysis, in addition to the well known CLAYFEN and CLAYCOP, bismuth(III) and chromium(III) nitrates supported on K10 montmorillonite (CLAYBIS, CLAYCHROM) appear to be active in our model reactions. If we compare the initial rates of these supported reagents observed at the same reaction temperature of 60°C:

$v_0(60°C) = 1.35 \times 10^{-2}$ mol/g*h for bismuth(III),
1.52×10^{-2} mol/g*h for iron(III),
2×10^{-3} mol/g*h for chromium(III) and
2.55×10^{-4} mol/g*h for copper(II),

the supported reagent obtained from Bi(III) nitrate showed an activity similar to that of CLAYFEN.

The series of the temperatures of beginning of decomposition:

$Bi(30) < Fe(35–50) < Cr(50) = Cu(50)$

and for the chemical activities $Bi(III) < Fe(III) < Cr(III) < Cu(II)$ follow the same pattern and we can conclude that the thermal stability of the hydrated nitrate determines the activity.

The chemical reactivity of these supported nitrates are then related to the low temperature of the nitrate decomposition, which accompanies the first water loss. The increasing order of the reactivity was similar to that of the series of the metals based on the nefelauxetic g factor [28-30]: $Zn(II) < Mn(II) < Ni(II) < Co(II) < Cu(II) < Fe(III) < Cr(III) < Bi(III)$ and this observation is consistent with the proposal that the reactivity is governed by the stability of the nitrates.

Several differences were observed between the decomposition of the pure salts and that of the supported ones. The starting phase of the decomposition is shifted towards lower temperatures in the case of supported nitrates, and some partial processes of decomposition are fused, due to the influence of the support. As a general rule, the nitrates which decompose at low temperature (Bi(III), Fe(III), Cr(III)) appear as more active in the oxidation of alcohols and nitration of phenols. However less active reagents can be used at higher temperature, thus the difference of reactivity can be partly compensated.

In some cases (Zn(II), Ni(II), Mn(II)) the melting point was lower than the temperature of the first step of decomposition. These metal nitrates show a lower activity if any. It is possible that the melting process was the cause of the inactivity of these metal nitrates, because the decomposition is then limited by the diffusion of the products in a liquid phase, which is expected to be slower than diffusion in gas phase.

It must be pointed out, that in any case, the rate of formation of NO^+ must equalize its rate of consumption by the oxidation or nitration of the organic substrate, then the temperature of use of the supported reagents must be adjusted to their reactivity. If the decomposition is fast, and the chemical reaction slow, nitrous oxide is lost and thus smaller yields will be obtained.

We must also emphasize that the decomposition of the supported nitrates begins at about 30–40°C, then can occur during preparation. The evaporation step has then to be done very carefully, at room temperature or below 35°C depending on the nature of the nitrate, in order to obtain a reproducible procedure of preparation. Carefully prepared supported reagents can be stocked in air and used without spontaneous decomposition and without loss of chemical activity even during six months. The spontaneous decomposition of CLAYFEN observed before is then probably related to the too high temperature of preparation.

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