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Catalytic effects on the oxidation of benzyl alcohol by montmorillonite-supported metal nitrates

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Summary — Iron(III) and copper(II) nitrates supported on K10 montmorillonite (Clayfen and Claycop) were prepared by impregnation. The metal nitrates were present on the support as crystalline hydrates, which were X-ray amorphous and had good dispersion. These supported metal nitrates were used as reagents for the oxidation of benzyl alcohol. Due to its high Brønsted acidity the clay support catalyzes the decomposition of finely dispersed nitrates which is the intermediate step of the chemical oxidation of the alcohol. The oxidation activity of these supported reagents depends on the oxygen content in the reactor gas atmosphere. Under an oxygen atmosphere metal nitrates can be used in a quantity less then stoichiometric. When the metal nitrate content is decreased at the surface of montmorillonite, part of the surface becomes free. In that case, with aromatic solvents, alkylation arises as a secondary reaction.

metal nitrate / montmorillonite / supported reagent / effect of reaction atmosphere / oxidation / benzyl alcohol / alkylation

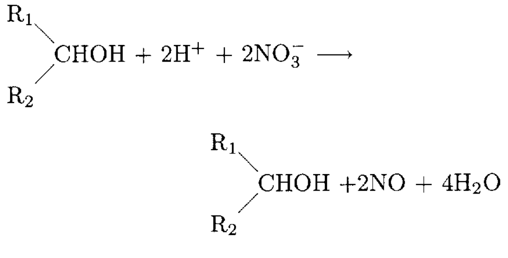
Résumé — Effets catalytiques au cours de l'oxydation de l'alcool benzylique par le nitrate de fer supporté sur montmorillonite désaluminée. *Des réactifs supportés (Clayfen et Claycop) ont été préparés par imprégnation de montmorillonite K10 par des nitrates de* Fe^{3+} *et de* Cu^{2+}*. Ces nitrates métalliques sont presque amorphes aux rayons X et se trouvent donc sur le support sous forme d'hydrates très dispersés, qui ont été utilisés comme réactifs pour l'oxydation de l'alcool benzylique. En raison de sa forte acidité de Brønsted l'argile utilisée comme support catalyse la décomposition du nitrate finement dispersé; cette décomposition est une étape intermédiaire de l'oxydation de l'alcool. La capacité de ces nitrates supportés pour l'oxydation de l'alcool benzylique dépend de la teneur en oxygène de l'atmosphère dans le réacteur. Sous oxygène les nitrates métalliques peuvent être utilisés en quantité sous-stœchiométrique. En diminuant la teneur en nitrate sur l'argile, une partie de la surface est libérée, et en présence de solvants aromatiques, l'alkylation apparait alors comme réaction secondaire.*

nitrate métallique / montmorillonite / réactif supporté / effet de l'atmosphère de réaction / oxydation / alcool benzylique / alkylation

Introduction

The direction and velocity of organic reactions can be modified if one of the reactants is adsorbed previously on an appropriate, by itself inactive, material. In this manner effects similar to that of catalysis can be achieved: milder reaction conditions may be used under which even sensitive materials can be handled, and better or special selectivities can be reached. An additional advantage is the easy work-up of a heterogeneous system and facilities for the isolation of products. A variety of supported reagents were described in recent works [1-5].

Metal nitrates deposited on a montmorillonite clay mineral are well-known cheap supported reagents [5]. A large number of applications of these supported nitrates have been described especially in synthetic chemistry [6-10]. The K10 clay-supported iron nitrate (Clayfen) was reported as efficient and selective for producing ketones from secondary alcohols, and aromatic aldehydes from the corresponding primary aromatic alcohols [5, 9, 11]. Iron nitrate in Clayfen was described as an anhydrous species, ie, an unstable acetone solvate of bidentate nitrate groups, and the role of the support was then to stabilize the solvate [8, 9]. In alcohol oxidations Clayfen acts as a source of nitrosonium ions (NO^+) and the reaction proposed in the literature [5, 9] is the following:



$$R_1R_2CHOH + 2H^+ + 2NO_3^- \longrightarrow R_1R_2CHOH + 2NO + 4H_2O \quad (1)$$

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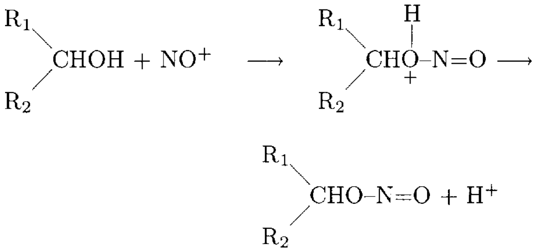
* Correspondence and reprints

followed by oxidation of NO to NO_2 in air. R_1 and R_2 are aliphatic or aromatic groups, but at least one of them is aromatic.

This proposal is supported by recent results on the oxidation of benzyl alcohol by oxygen in strongly acidic aqueous solutions in the presence of nitrous acid as catalyst reported by Levina and Trusov [13, 14]. NO^+ was proposed as a key component of the oxidation reaction. The nitrite would then be a reaction intermediate, and the acidity of the K10 clay support is then required for the decomposition of this nitrite intermediate into the carbonyl product, in an acid-catalyzed pathway [9].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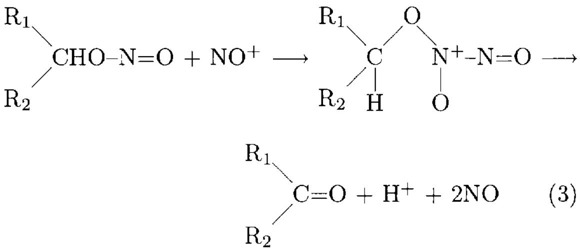
(3)

Recently Kim and coworkers reported that montmorillonite-supported potassium permanganate is also a powerful reagent for the oxidation of alcohols (eg, oxidation of cyclohexanol to cyclohexanone, benzyl alcohol to benzaldehyde, octan-1-ol to octanal, and various substituted primary aromatic alcohols) [12]. The reactions were carried out under nitrogen by sonication of the reaction mixture. The catalytic activity of unsupported $KMnO_4$ was found to be very low. Unfortunately the structural properties of this supported reagent and the mechanism of the oxidation were not determined, and it is impossible to conclude on a possible cause of the support effect of montmorillonite in these reactions.

In our recent work [15–18], various clay-supported metal nitrates were investigated, ie, Bi(III), Fe(III), Cr(III), Cu(II), Mn(II), Ni(II), Co(II) and Zn(II) nitrates supported on different K clays from Süd-Chemie or on Hungarian bentonite. We established that the metal nitrates were present on the support not as acetone solvates, but as crystalline hydrates containing all the crystallization water of the nitrates [16, 17]. Some differences were observed between the decomposition of pure and supported metal nitrates. It was established that for supported nitrates the decomposition was shifted towards lower temperatures and some partial decomposition processess were fused, due to the influence of the support [16]. It was reported [17] that the thermal stability of metal nitrates determines the chemical activity of the supported reagent. Temperature produces two different effects: its increase during the chemical application increases not only the rate of the chemical reaction (oxidation of benzyl alcohol for instance) but also the decomposition of nitrates which produces the active agent for oxidation or nitration [17]. It was also shown [18] that the surface area of the support determines the dispersion of the deposited metal nitrate, and that the chemical activities of these clay-supported reagents are proportional to the surface area of the support. Some evidence was recently given [18] that the protonic acidity of the support is also a very important factor for the chemical activity of clay-supported metal nitrates.

Nevertheless several questions are still open for the application of these reagents in oxidation reactions related to the mechanism of reaction and the oxygen balance: for example, is it an oxidation by the nitrate or is there an intervention of the oxygen from the gas phase? Some of them are studied in the present work, including the comparison of the supported reagents obtained from Fe and Cu nitrates (Clayfen and Claycop) for benzyl alcohol oxidation. We also studied the oxidation of benzyl alcohol to the corresponding carbonyl compound using a quantity of clay-supported nitrate lower than that proposed by Laszlo [9]. Another aim of this work was to examine the influence of the oxygen content of the reaction atmosphere in order to study its influence on the rates of oxidation. Finally we determined the oxidation capacity of these supported reagents, defined by the number of moles of alcohol oxidized per mole of metal nitrate engaged in the process. In particular we studied the influence of the amount of nitrate deposited on the support on the reactivity.

Experimental section

Characteristics of the supports used for the preparation of supported reagents

K10 montmorillonite (Süd-Chemie): Specific surface area 229 m^2/g, 90% of particles < 0.065 mm. This is an acidic support since the pH of a 10% suspension in water is 4.5.

Al_2O_3 (Merck): Specific surface area 122 m^2/g, particle size 0.063–0.200 mm. Alumina is a neutral support, as judged from the pH of a 10% suspension in water: 7.3.

SiO_2 (Merck): Specific surface area 476 m^2/g, particle size 0.063–0.200 mm. Silica is also a neutral support and the pH of a 10% suspension in water is 7.3.

Preparation of the supported reagents [5, 15, 16]

The hydrated metal nitrate or chloride (3.33 mmol of metallic salt for 1.8 g support) was added to acetone (125 mL) in a 0.25 L evaporating flask (table I). The mixture was stirred vigorously for 15 min. In the case of iron nitrate, dissolution was not complete and a yellow-brown suspension was observed. The support (10 g) was added in small amounts and stirring continued for another 15 min. The solvent was then removed from the resulting suspension under reduced pressure (rotary evaporator) on a water bath, at a temperature not exceeding 30 °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 drying continued. The dry precipitate was powdered. This procedure yields a floury powder, the chemical composition of which corresponds to a supported hydrated metal nitrate [16].

Table I. Preparation of the supported reagents.

Metallic salt	*Support*	*Supported reagent*
5.02 g $FeCl_3 \cdot 6H_2O$	10 g K10	$FeCl_3 \cdot 6H_2O$/K10
7.50 g $Fe(NO_3)_3 \cdot 9H_2O$	10 g K10	$Fe(NO_3)_3 \cdot 9H_2O$/K10 (Clayfen)
7.50 g $Fe(NO_3)_3 \cdot 9H_2O$	10 g alumina	$Fe(NO_3)_3 \cdot 9H_2O$/alumina
7.50 g $Fe(NO_3)_3 \cdot 9H_2O$	10 g silica	$Fe(NO_3)_3 \cdot 9H_2O$/silica
6.66 g $Cu(NO_3)_2 \cdot 3H_2O$	10 g K10	$Cu(NO_3)_2 \cdot 3H_2O$/K10 (Claycop)

Chemical reactions

Different amounts of supported reagent (indicated in the captions of tables and figures) were added to 1.08 g (10 mmol) benzyl alcohol diluted in 50 mL of solvent. The reactions were carried in a batch reactor at a temperature of 60 °C (Clayfen) or 75 °C (Claycop). The chemical analyses were monitored by gas chromatography using a column consisting of Celite impregnated with a mixture of PEG 1500, SE30 and THEED in the ratio 2:2:1.

Results

Effect of the reaction atmosphere

We report here the results obtained with Clayfen in different reaction atmospheres (table II). We must first notice that over-oxidation of benzaldehyde to benzoic acid was not observed, which means that the reaction is 100% selective for benzaldehyde.

Table II. Effect of the atmosphere of reaction for the oxidation of benzyl alcohol with Clayfen.

	Yield of benzaldehyde (%)		
Solvent	*Under N_2*	*Under air*	*Under O_2*
Hexane	42		
Hexane		75	
Hexane			79
Benzene	77		
Benzene		85	
Benzene			100
Toluene	82		
Toluene		93	
Toluene			98

Reaction temperature: 60 °C, reaction time: 3 h, benzyl alcohol: 10 mmol, Clayfen: 1.57 g (0.67 g = 1.66 mmol iron nitrate = 5 mmol NO_3^-, on 0.9 g support), molar ratio NO_3^-/alcohol = 0.5.

Two different trends were observed: (1) the final yields were higher in aromatic solvents that in heptane, which can be accounted for by a better solubility of the substrate; and (2) the reaction atmosphere had a significant influence. If the reaction involved only the nitrate groups, as written in equation (1), an NO_3^-/alcohol ratio of 0.5 could not result in benzaldehyde yields higher than 75% (0.5·(3/2)·100). As can be seen from table II, in practically all the cases the yields exceed the 75% level.

Moreover the yields increase with the oxygen content in the reaction atmosphere. This effect of the atmosphere on the yields is higher in aromatic solvents than in heptane, which probably reflects a higher solubility of oxygen in aromatic solvents. These results demonstrate that gaseous oxygen plays an important role in the system, due to redox catalysis by Fe^{3+} ions. It can be pointed out however that the results obtained under an N_2 atmosphere using toluene as solvent are also slightly above 75%, which suggests that Fe^{3+} can be at least partly reduced in the reaction.

We observed a change of color of the reagents during the reaction in aromatic solvents, especially when the reaction was performed in air or oxygen. This color was red in benzene and stable in a closed cell even for some days. One of our hypotheses was the appearance of radicals, but we could not confirm the existence of radicals by ESR by performing the reaction in situ in an ESR apparatus or by applying radical trapping. Another hypothesis was the formation of complexes analogous to ferrocenes [19–21], but the reaction conditions were not as extreme as those recently proposed for the production of this type of complexes [19, 20] and their appearance is not very probable. The cause of this color effect is under investigation.

We studied the same effect of the atmosphere in the case of oxidation by Claycop (table III). This study was carried out at a higher temperature (75 °C) because of the higher thermal stability of copper nitrate established by thermal analysis [16, 17]. We have recently published [15, 16] that Claycop is less active than Clayfen in the reactions of oxidation of alcohols and nitration of substituted phenols. The results presented here show the same chemical trends, and the oxygen effect is also less significant using the Claycop reagent. If we start with a molar ratio nitrate/alcohol = 0.5, then the maximum yield according to the formula is 75%. Using Claycop only a few observed yields are in conflict with the mechanism proposed by Laszlo.

Table III. Effect of the atmosphere of reaction for the oxidation of benzyl alcohol with Claycop.

	Yield of benzaldehyde (%)		
Solvent	*Under N_2*	*Under air*	*Under O_2*
Heptane	46		
Heptane		59	
Heptane			66
Benzene	58		
Benzene		70	
Benzene			100
Toluene	53		
Toluene		85	
Toluene			91

Reaction temperature: 75 °C, reaction time: 3 h, benzyl alcohol: 10 mmol, Claycop: 1.50 g (0.60 g = 1.66 mmol copper nitrate, 3.33 mmol NO_3^-, on 0.9 g support), molar ratio NO_3^-/alcohol = 0.5.

Using aromatic solvents for the reaction of Claycop the color of the reaction mixture turns to violet, but unfortunately, as for Clayfen, we could not identify the radicals.

Comparison of different supports

The effect of the support on the oxidizing capacity of supported iron nitrate was investigated on K10 montmorillonite, silica and alumina. Iron chloride supported on K10 was also prepared, to investigate the possible influence of the reducibility of Fe^{3+} cations in the oxidation of benzyl alcohol under an atmosphere of air. The results are presented in figure 1. At 60 °C iron nitrate supported on K10 was the most active supported reagent, but supported iron chloride also exhibited a fairly high activity. The good activity of iron chloride can be accounted for by the reduction of iron cations by benzyl alcohol, or redox catalysis by Fe cations.

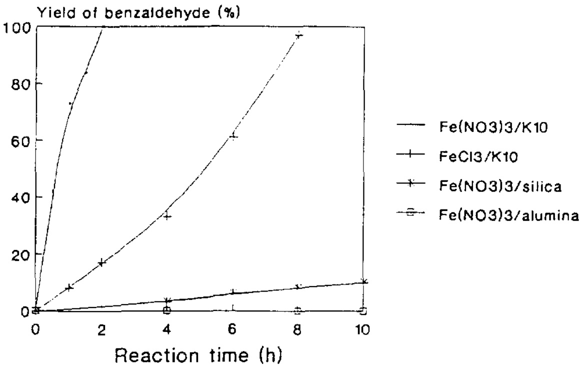

Fig 1. Yields of benzaldehyde as a function of time at 60 °C, for the oxidation of benzyl alcohol by different supported reagents. Benzyl alcohol: 10 mmol, heptane as solvent: 50 mL, $Fe(NO_3)_3$/K10 2.10 g (6.7 mmol NO_3^-), $Fe(NO_3)_3$/silica 2.10 g (6.7 mmol NO_3^-), $Fe(NO_3)_3$/alumine 2.10 g (6.7 mmol NO_3^-), $FeCl_3$ 1.80 g (2.23 mmol Fe).

Iron nitrate supported on non-acidic silica or alumina was less active in spite of the high specific surface areas of these supports. This result points out the influence of acidity which is believed to catalyze the decomposition of nitrates. At a higher temperature (90 °C) the alumina-supported iron nitrate was more active, but less than K10- or silica-supported iron nitrates.

Oxidizing capacity of supported iron nitrate

It follows from the foregoing that K10-supported iron nitrate possesses a very high activity in oxidation reactions. The oxidizing capacity of iron nitrate was investigated by decreasing the quantity of iron nitrate at the surface of K10 montmorillonite. If benzene is used as solvent for the oxidation of benzyl alcohol, and the acid sites of montmorillonite are accessible, then a second reaction can occur: alkylation of benzene with benzyl alcohol, which produces diphenyl methane (fig 2).

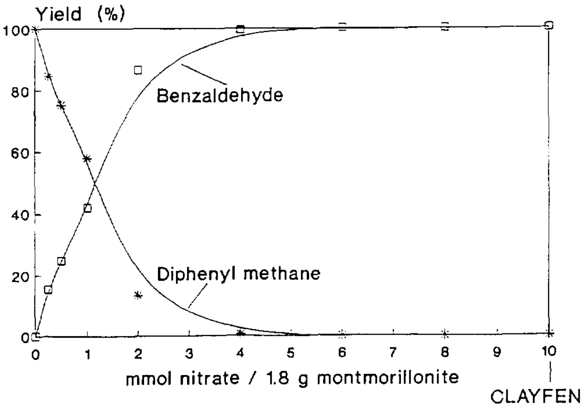

Fig 2. Final yields reached at different iron nitrate contents. Competition between the oxidation of benzyl alcohol to benzaldehyde and the alkylation of benzene by benzyl alcohol to diphenylmethane. Reaction temperature: 60 °C, benzyl alcohol:10 mmol, solvent: benzene (50 mL), support 1.8 g K10 montmorillonite.

The standard reagent contains 10 mmol NO_3^- (or 3.33 mmol iron nitrate) for 1.8 g of K10 montmorillonite support. In this case we never observed alkylation of benzene, which is attributed to the fact that the nitrate probably completely covers the surface of montmorillonite. The other extreme case is the pure K10 montmorillonite without iron nitrate, where we observe a total alkylation by benzyl alcohol. To study this secondary support effect and the competition of these two reactions, we prepared different supported reagents with the same method as described in the *Experimental section* but changed the quantity of iron nitrate deposited from 10 mmol to 0.25 mmol (the quantity of support was the same in all cases) (table IV). As can be seen in table IV we observed high yields of benzaldehyde in spite of lower quantities of iron nitrate.

Above 6 mmol of nitrate/1.8 g support, we observed only oxidation; the acid sites were apparently not accessible and the montmorillonite surface was covered by the nitrate. When the metal nitrate content on the surface of montmorillonite decreased below 4 mmol/1.8 g, alkylation arose, which suggests that part of the surface became free. A further decrease in the coverage of the montmorillonite surface causes an increase in the yield of diphenylmethane.

For a level $\leqslant$ 4 mmol nitrate/1.8 g support, we observed competition between two reactions. We show in table IV (5th column) the calculated excess benzaldehyde yield which cannot be explained by the consumption of nitrates represented in equation (1). The calculated oxidizing capacity of the reagents was also determined (table IV, 6th column). A value of 100% represents the oxidizing capacity of the reagent if all the nitrate is consumed in the oxidation. The values which are above 100% cannot be explained on the base of nitrate consumption only. In that case ferric ions must catalyze the reaction using the oxygen in the atmosphere.

In table V we compare the initial rates observed for both oxidation and alkylation reactions of benzaldehyde. The experimental results for the reagent contain-

Table IV. Oxidation of benzyl alcohol by supported reagents containing different amounts of nitrate at the surface.

Amount of nitrate on 1.8 g support (mmol)	*Conversion of benzyl alcohol (%)*	*Yield of benzaldehyde (%)*	*Yield of diphenylmethane (%)*	*Benzaldehyde yield above stoichiometric (%)*	*Oxidizing capacity related to the nitrate contained in the reagent (%)*
10	100	100	0	0	100
8	100	100	0	0	100
6	100	100	0	11	100
4	100	99.5	0.50	39.5	166
2	100	86.6	13.4	56.6	288
1	100	42.0	58.0	27.7	280
0.5	100	24.6	75.4	17.1	328
0.25	100	15.4	84.6	11.6	410
0	100	0	100	–	–

Reaction temperature: 60 °C, benzyl alcohol: 10 mmol, solvent: benzene (50 mL), support 1.8 g K10 montmorillonite.

Table V. Comparison of the initial rates at low contents of iron nitrate.

Amount of iron nitrate on 1.8 g support (mmol)	*Initial rate of oxidation (formation of benzaldehyde) $\cdot 10^4$ mol/h·g reagent*	*Initial rate of alkylation (formation of diphenylmethane) $\cdot 10^4$ mol/h·g reagent*
10	95.5	–
2	33.3	0.7
1	12.4	2.3
0.5	11.2	5.6
0.25	9.8	6.2
0	–	6.6

ing 1 mmol nitrate on 1.8 g support are presented in figure 3 as an illustration of the general situation. The alkylation follows a zero order in function of the concentration of alcohol; thus the rates of alkylation reported in table V are rate constants. The curves of figure 3 can be analyzed by linear regression to obtain the rate constants in a reaction scheme:

$$\Phi\ CH_2OH + Fe(NO_3)_3 \xrightarrow{k_1} \Phi\ CHO$$

$$\Phi\ CH_2OH + C_6H_6 \xrightarrow{k_2} \Phi\ CH_2\Phi$$

The fit gives rate constants $k_1 = 3.97 \times 10^{-3}$ mol/min and $k_2 = 3.8 \times 10^{-6}$ mol/min/g. The value of k_2 is in accord with the experimental value of 2.3×10^{-3} h^{-1} obtained from the initial rate. The rate is three orders of magnitude higher for oxidation than for alkylation; thus alkylation starts only when oxidation is finished.

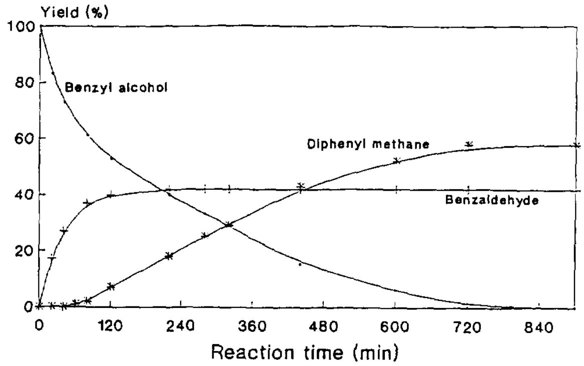

Fig 3. Competition between the oxidation of benzyl alcohol to benzaldehyde and the alkylation of benzene by benzyl alcohol to diphenylmethane; variation of the yield as a function of time, using a K10-supported iron nitrate reagent containing 1 mmol NO_3^- on 1.8 g support. Reaction temperature: 60 °C, benzyl alcohol: 10 mmol, solvent: benzene (50 mL), support: K10 montmorillonite.

Discussion

K10 is an industrial product of Süd-Chemie obtained by acidic treatment of a Bavarian bentonite. It has lost the typical structure of montmorillonite, and has been converted to a mesoporous solid (average pore size: 56 Å) of large surface area (229 m^2/g) which possesses high acidity [22].

In this work we observed in numerous cases oxidation yields higher than those accounted for by the stoichiometric reaction of nitrates supposed earlier [9]. We propose that in this supported system the high surface area of the support provides a good dispersion for metal salts and the Brønsted acidity of support catalyzes the decomposition of nitrates, which produces the NO^+ as an active agent for oxidation. The mechanism of decomposition of supported metal nitrates [16, 17], has been reported recently, showing the appearance of NO in cases both of iron and copper nitrates. However the relatively high oxidation capacity observed when the metal nitrates are used in a quantity less than stoichiometric also indicates other effects. When oxygen is present in the reaction atmosphere, and the metal cations of the supported reagent can be reduced, the oxidizing capacity of the cations is not negligible. This proposal is supported by the results obtained with supported iron chloride, which appears as an efficient oxidation agent. The dispersion appears to have a noticeable effect on the reducibility of Fe^{3+} cations since the capacity for oxidation increases at low nitrate contents, therefore at high dispersion. The conversion of benzyl alcohol to benzaldehyde does not however reach a true catalytic regime in these experimental conditions since the turnover remains below 4.

We can conclude that the use of non-acidic supports (silica, alumina) is not very advantageous for the preparation of supported iron nitrate. If we compare the results obtained with silica and alumina, we see that a good dispersion of metal nitrate due to a high surface area of the support facilitates the decomposition of metal nitrate, and provides a good chemical activity at higher temperatures. However, it must be pointed out that the absence of Brønsted acidity cannot be compensated by a higher specific surface area, since the use of silica results in an activity lower than that obtained with K10, which exhibits a lower surface area but a high Brønsted acidity.

Decreasing the iron nitrate content on K10, part of the surface becomes free, and using benzene as solvent the possibility of alkylation as secondary reaction arises. Alkylation begins when oxidation is practically finished (fig 3). The higher reactivity for oxidation suggests that the competition between NO^+ and H^+ for the reaction on benzylalcohol is favorable to NO^+, therefore alkylation is only observed when the nitrate is decomposed.

Conclusion

The high activity of K10-supported iron nitrate reagents in alcohol oxidation reactions is related to three simultaneous factors: (i) the variable valence of iron; (ii) the presence of salt in the form of a hydrated nitrate very well dispersed on the surface; and (iii) the acidity of the support.

Acknowledgments

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