Low temperature selective catalytic oxidation and nitration using environmentally friendly reagents

Sándor Békássy,*[,a] Tivadar Cseri,†[,a] Márta Horváth,[a] János Farkas[a] and François Figueras[b]

[a] *Technical University of Budapest, Department of Organic Chemical Technology, H-1521 Budapest, Hungary*
[b] *Institut de Recherches sur la Catalyse (CNRS UPR 5401), 2 Avenue Albert Einstein, F-69626 Villeurbanne, France*

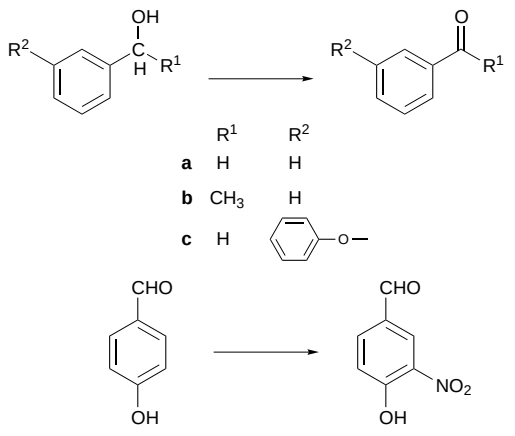
The selective oxidation of benzyl, phenylethyl and phenoxybenzyl alcohols can be performed using metallic nitrates supported on clays. It is shown here that similar or better yields can be achieved by simple addition of iron, bismuth or copper nitrates and a dealuminated or a natural clay to the reaction mixture, instead of their supported equivalent. The acid catalytic role of the clay is suggested by its concentration effect on the reaction rate. These observations open up new opportunities for easy scale-up of selective oxidation of fragile organic compounds such as phenoxybenzyl alcohol. The selective nitration of 4-hydroxybenzaldehyde also gives good yields with the same catalytic system.

Oxydation et nitration catalytiques sélectives et à basse température avec réactifs respectueux de l'environnement. L'oxydation sélective d'alcools benzylique, phényléthylique et phénoxybenzylique par des nitrates métalliques catalysée par des argiles acides est comparée à la réaction obtenue avec des réactifs supportés. Des rendements similaires ou supérieurs, voisins de 100%, sont obtenus avec des nitrates de fer, bismuth ou cuivre. Des argiles naturelles peuvent aussi être utilisées comme catalyseur dans ce procédé. Ces systèmes catalytiques peuvent être utilisés avec des composés fragiles comme l'alcool phénoxybenzylique et sont faciles à extrapoler à grande échelle. La nitration très sélective du 4-hydroxybenzaldéhyde donne aussi d'excellents rendements avec ce système catalytique.

Supported reagents have been widely used in organic synthesis for some 25 years and new systems have been recently proposed.[1–3] Some of these reagents have found industrial applications[4] and their importance is likely to increase as a result of new environmental demands and the drive towards clean technologies in the manufacture of pharmaceutical and fine chemical intermediates. They have been designed for processes usually operating in the liquid phase at low temperatures for the conversion of fragile substrates, for which heterogeneous catalysis can hardly be used. The use of supported reagents has thus recently attracted much attention.[4–11] Clay-supported metallic nitrates constitute a special class of these reagents,[8,9] particularly interesting in the field of oxidation and nitration, which use environmentally unfriendly agents such as chromium salts or sulfonitric and nitric acids. These supported reagents may, however, lack stability and probably for this reason are rather irreproducible in their preparation and in their chemical applications. For instance, iron(III) nitrate was proposed to form an unstable acetone solvate by dissolution in acetone; its deposition on a support first aimed to stabilize this explosive solvate and this instability could then account for the difficulty of preparation.[8] It can be inferred that the problems are even more complex on the industrial scale.

The physicochemical characterization by infrared spectrometry, thermal and thermoemanation analyses as well as X-ray diffraction of several metallic nitrates (Fe, Cu, Bi, Cr, Mn, Ni, Zn and Co) supported on a commercial dealuminated clay (K10 from Süd Chemie) led, however, to the conclusion that these nitrates are in fact hydrated salts and nearly amorphous due to the small size of the crystals.[12–15] Their reactivity is controlled by the decomposition kinetics of the nitrate and the support, by its acidity, acts as a catalyst for this decomposition.[16]

In this hypothesis of a reaction catalyzed by the clay, a new process can be imagined in which the metallic nitrate is added directly to the reaction medium as a normal reagent (*in situ* preparation method), instead of being introduced previously into the clay by a complex procedure. We illustrate here the possibilities of this new method for the oxidation of alcohols and nitration of phenols (Scheme 1), in comparison with the usual process based on the corresponding supported reagents.



Scheme 1

* Fax: (+36) 1 463 3648; E-mail: bekas@oct.bme.hu
† Present address: Institut Français du Pétrole, F-92506 Rueil-Malmaison, France.

Experimental

Conventional preparation method of the supported reagents[8,9,12]

The 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 hydrated metal nitrate (in the case of iron, chromium and bismuth nitrate suspensions were observed). K10 clay (15 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, not exceeding 30–35 °C.[12] 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 continued. The dry precipitate was powdered. The procedure yields a floury powder.

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

Reaction conditions

The oxidation and nitration reactions were carried out in a batch reactor. The oxidation reactions were monitored by gas chromatography using a column consisting of Celite impregnated with a mixture of PEG 1500, SE-30 and THEED in a 2 : 2 : 1 ratio. The nitration reactions were monitored by HPLC (C_{18} reversed phase column, UV detector at 254 nm, methanol : water as eluent).

The reaction procedure was as follows: (*a*) with the supported reagents, different amounts of previously prepared reagent (indicated in the captions of tables and figures) were added to 10 mmol of aromatic alcohol or substituted phenol compounds, diluted in 50 ml of solvent, at room temperature, followed by heating to the reaction temperature; (*b*) in the catalytic method, the same amounts of clay, metal nitrate and substrate as used above were added to the solvent at room temperature; the mixture was then heated to the reaction temperature. In some cases the amount of clay was reduced.

Results

K10 alone shows no activity for the two reactions investigated here: oxidation of aromatic alcohols and nitration of phenols. The reactivities of the pure hydrated metal nitrates determined in the oxidation of benzyl alcohol at 60 °C are reported in Table 1. Only iron(III), bismuth(III) and chromium(III) nitrates show measurable activity, which is rather low since the yield is a maximum of 40–60% after 12 h.

The reactivities of the conventional supported reagents have been compared with the catalytic reaction: the results for the oxidation of benzyl alcohol by bismuth(III) nitrate are reported in Table 2. Since the toxicity of solvents is also an important parameter for industrial practice, hexane and benzene were compared. Benzaldehyde is the only product of the reaction, obtained with 100% selectivity in all cases.

Table 1 Oxidation of benzyl alcohol by pure metallic nitrates[a]

Salt	Quantity/g[b]	Reaction time/h	Yield benzaldehyde/%
$Fe(NO_3)_3 \cdot 9H_2O$	1.34	19.5 (13)	63.5 (54)
$Cu(NO_3)_2 \cdot 3H_2O$	1.21	12	4
$Bi(NO_3)_3 \cdot 5H_2O$	1.65	12.5	61
$Cr(NO_3)_3 \cdot 9H_2O$	1.32	20.5 (12)	50 (41)
$Zn(NO_3)_2 \cdot 6H_2O$	1.48	12	0
$Co(NO_3)_2 \cdot 6H_2O$	1.49	12	0
$Mn(NO_3)_2 \cdot 4H_2O$	1.25	12	0
$Ni(NO_3)_2 \cdot 6H_2O$	1.49	12	0

[a] Reaction temperature 60 °C, solvent benzene, molar ratio NO_3^- : alcohol = 1 : 1. [b] This quantity is equal to 10 mmol of the salt.

The main difference concerns the rates: similar rates can be observed in the catalytic process or using the supported reagent, and higher rates are observed when using an acid catalyst (K10) instead of a neutral bentonite. The nature of the solvent has also some influence since lower rates are obtained with hexane. This can be attributed to a lower solubility of the nitrate.

A further comparison of the catalytic and the conventional processes is reported in Table 3, which includes the results obtained with bismuth(III), iron(III), copper(II) and chromium(III) nitrates. An interesting observation is that under these conditions (Tables 2 and 3), natural bentonites can also be used with reasonably good results, which requires the creation of acidity by interaction with the metal nitrates. It is well-known that cation exchange in zeolites can occur in the solid state when using chlorides for example.[17] It can be pointed out here that both the clay and the nitrate are hydrated; thus the mobility of the cations at the surface is ensured by the water layer. The introduction of multivalent cations on zeolites and clays promotes acidity[18] and it is likely that the acidity required by the reaction is provided by the exchange of Fe^{3+}, Bi^{3+} or Cu^{2+} cations into the natural bentonite.

These nitrates react very fast at 60 °C; the rate is so fast that it is limited by the diffusion of the reactants in the pores of the mesoporous K10 clay. The oxidation of benzyl alcohol can also be performed at room temperature; under these conditions a slower reaction is observed but the final yield is practically the same. This high reactivity permits fragile substrates or polyfunctional compounds, which could be fragmented at higher temperatures, to be converted.

Table 2 Oxidation of benzyl alcohol with different systems based on bismuth nitrate to give benzaldehyde (% yield)[a]

	Reaction time/h							
	In benzene				In hexane			
System [b]	1	2	3	4	1	2	3	4
$Bi(NO_3)_3 \cdot 5H_2O$	—	—	35	52	46	50	52	52
Bi + bentonite	61	74	81	87				
Bi/bentonite	81	91	95		68	75	81	
Bi + K10	91	95	97		79	85	92	94
Bi/K10	96	98			95	98		

[a] Reaction temperature 60 °C, molar ratio NO_3^- : alcohol = 1 : 1. [b] Bi/K10 stands for the supported reagent, prepared previously, and Bi + K10 for the mixture of nitrate and clay added simultaneously to the reaction medium (catalytic or *in situ* method).

Table 3 Benzaldehyde yields (%) as a function of time for the oxidation of benzyl alcohol by different couples of metallic nitrate and clay (catalytic method)

	Reaction time/h							
System	1	2	3	4	6	8	10	12
Bi + K10[a]	91	95	97					
Bi + bentonite[a]	61	74	81	87				
Bi/K10[b]	4	9	24	44	68			
Bi + K10[b]	1	—	3	—	10	31	68	87
Fe + K10[a]	92	98						
Fe + bentonite[a]	40	—	85					
Fe/K10[b]	3	—	—	10	—	48	54	56
Fe + K10[b]	—	1	—	5	—	51	55	57
Cu + K10[a]	10	28	60	82				
Cu + bentonite[a]	—	51	—	65				
Cr + K10[a]	83	96	98					
Cr + bentonite[a]	26	—	43					

[a] At 60 °C in benzene, using a molar ratio NO_3^- : alcohol = 1 : 1. [b] At room temperature in benzene, using a molar ratio NO_3^- : alcohol = 1 : 1.

Further illustrations of the effectiveness of the catalytic systems are the oxidations of 1-phenylethyl alcohol (Table 4) and the industrially interesting *m*-phenoxybenzyl alcohol (Fig. 1) to the corresponding carbonyl compounds. In all these cases a complete selectivity to the carbonyl compound is observed, which is indeed remarkable.

Table 4 Acetophenone yields (%) as a function of time for the oxidation of 1-phenylethyl alcohol by iron and bismuth nitrates[a]

	Reaction time/h					
System	0.5	1	2	3	3.5	4
K10						0
Fe nitrate		9	12	20		25
Fe + K10	76	83	91	95	—	97
Fe/K10	80	89	93	—	95	—
Bi nitrate		11	20			35
Bi + K10	73	81	96	—	98	—
Bi/K10	72	78	85	—	88	

[a] Reaction temperature 60 °C, solvent benzene, molar ratio NO_3^- : alcohol = 1 : 1.

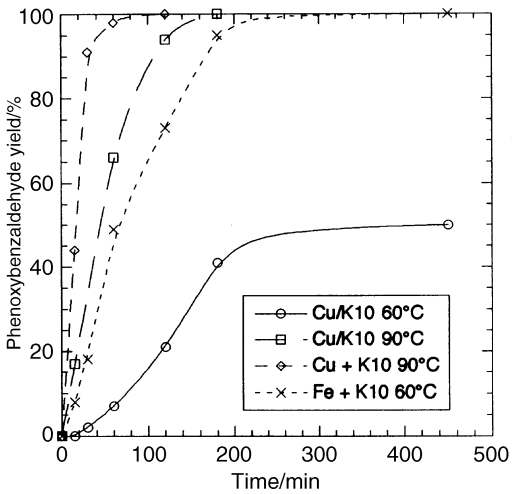


Fig. 1 Yields of *m*-phenoxybenzaldehyde obtained in the oxidation of *m*-phenoxybenzyl alcohol by copper and iron nitrates in heptane, molar ratio NO_3^- : alcohol = 0.67 : 1

The K10 clay can be repeatedly used as catalyst. An example is the oxidation of benzyl alcohol in benzene at 60 °C: K10 (after washing with the solvent and without any special regeneration) and a new portion of bismuth nitrate gives the same yield, with a somewhat lower reaction rate only in the third cycle.

The nitration of substituted phenols is also possible: the good reactivity at low temperatures of these metallic nitrates in the presence of K10 clay as a catalyst allows the nitration of substituted phenols to be performed with high selectivity, as illustrated in Table 5.

Because of the catalytic effect of the clay the amount of K10, at a constant amount of metallic nitrates, can be reduced down to a proportion that cannot be reached by the usual supported reagent technique. With the diminished clay quantities the same chemical yield can be obtained, although the reaction rate decreases somewhat.

Fig. 2 illustrates the effect of the amount of K10 on the oxidation of benzyl alcohol. The K10 quantity necessary for a reasonable reaction rate depends on the metal. The more reactive the metallic nitrate, the lower the amount of K10 needed to induce a fast increase of the oxidation rate. In the case of Bi, the addition of 5% of K10 has no effect relative to the pure nitrate, but the introduction of 10% of the amount used in the supported reagent results in a practically complete conversion, within 3 h. With the less active iron(III) nitrate, a less sharp difference can be observed between 25 and 50% of K10.

Table 5 Yields of 3-nitro-4-hydroxybenzaldehyde obtained in the nitration of 4-hydroxybenzaldehyde by metallic nitrates used either supported or simply added to the reaction mixture[a]

System	Yield/%
Bi + K10	85[b]
Bi/K10	77[b]
Fe + K10	100[c]
Fe/K10	94[c]
Cu + K10	87[b]
Cu/K10	58[b]
Cr + K10	87[b]
Cr/K10	84[b]

[a] Reaction temperature 60 °C, solvent toluene, molar ratio NO_3^- : 4-hydroxybenzaldehyde = 1.3 : 1. [b] Reaction time of 4 h. [c] Reaction time of 3 h.

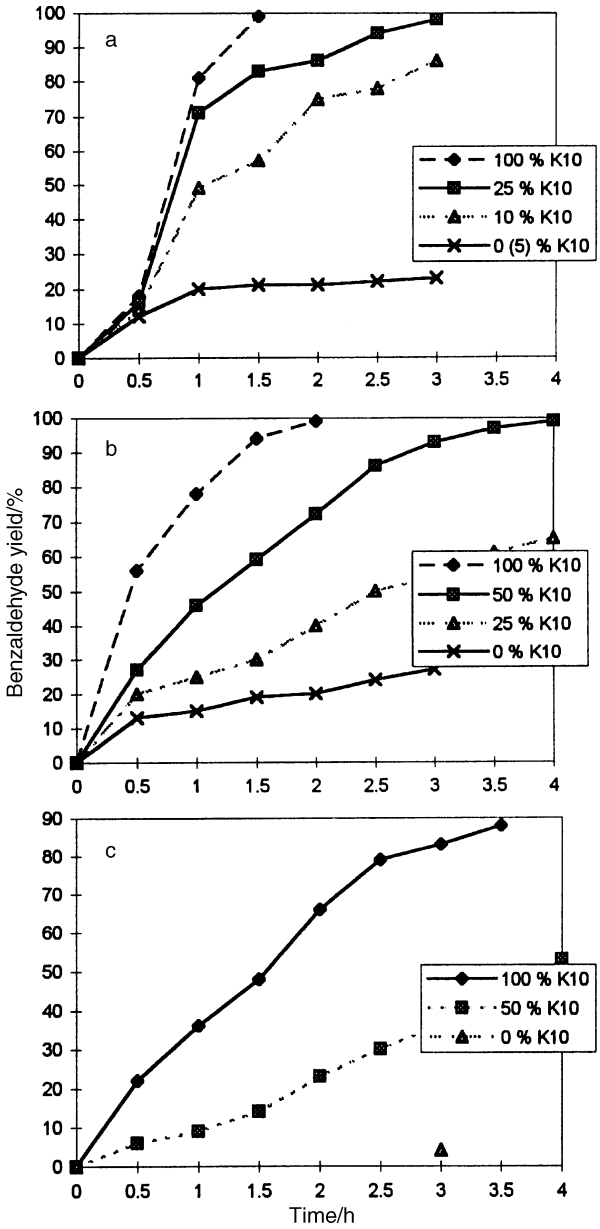


Fig. 2 Benzaldehyde yields as a function of time and the amount of K10 for the oxidation of benzyl alcohol by different couples of metallic nitrate and clay (catalytic method). (a) $Bi(NO_3)_3$, (b) $Fe(NO_3)_3$, (c) $Cu(NO_3)_2$. Reaction temperature 60 °C, solvent benzene, molar ratio NO_3^- : alcohol = 0.67 : 1

The reduction of the K10 amount is not so advantageous in the nitration of 4-hydroxybenzaldehyde in toluene at 60 °C. After a very quick initial the process becomes slower, but total conversion and selectivity can be obtained also with 25–50% of K10.

In conclusion, this catalytic process based on metallic nitrates in the presence of dealuminated K10 clay allows high yields in the selective oxidation of alcohols and nitration of phenol compounds to be reached. The basic chemistry involved in these reactions is that formerly described for the supported reagents, but the type of process proposed here bypasses the difficulties generally encountered in the preparation of these supported reagents, could eventually be scaled-up rather easily, and thus open up the possibility of industrial applications.

Acknowledgements

T. Cseri thanks the Foundation Varga József of the Technical University of Budapest for a grant. The financial support of OTKA (T-015673 and T-016305) and of the Ministry of Education and Culture (MKM 757) is also gratefully acknowledged.

References

1 H. G. Posner, *Angew. Chem.*, 1978, **90**, 527.
2 A. McKillop and D. W. Young, *Synthesis*, 1979, 401.
3 G. Bram, E. d'Incan and A. Loupy, *Nouv. J. Chim.*, 1982, **6**, 689.
4 T. W. Bastock and J. H. Clark, in *Speciality Chemicals*, ed. B. Pearson, Elsevier, London-New York, 1991, p. 383.
5 *Preparative Chemistry Using Supported Reagents*, ed. P. Laszlo, Academic Press, San Diego, CA, 1987.
6 J. H. Clark, A. P. Kybett and D. J. Macquarrie, *Supported Reagents: Preparation, Analysis and Applications*, VCH, New York, 1992.
7 *Solid Supports and Catalysts in Organic Synthesis*, ed. K. Smith, Ellis Horwood-PTR Prentice Hall, New York-London, 1992.
8 A. Cornélis and P. Laszlo, *Synthesis*, 1985, 909.
9 P. Laszlo and A. Cornélis, *Aldrichimica Acta*, 1988, **21**, 97.
10 L. Delaude, P. Laszlo and K. Smith, *Acc. Chem. Res.*, 1993, **26**, 607.
11 J. H. Clark, S. R. Cullen, S. J. Barlow and T. W. Bastock, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1117.
12 S. Békássy, T. Cseri, G. Kenessey, G. Pokol, K. Tomor and G. Liptay, *J. Therm. Anal.*, 1993, **40**, 1285.
13 T. Cseri, S. Békássy, G. Kenessey, G. Liptay and F. Figueras, *Thermochim. Acta*, 1996, **288**, 137.
14 T. Cseri, S. Békássy and F. Figueras, *Bull. Soc. Chim. Fr.*, 1996, **133**, 547.
15 T. Cseri, S. Békássy, G. Kenessey, G. Liptay and V. Izvekov, Symposium on Thermal Analysis, Sopron, Hungary, 1995.
16 S. Békássy, T. Cseri, Z. Bódás and F. Figueras, *New J. Chem.*, 1996, **20**, 357.
17 H. G. Karge and H. K. Beyer, in *Studies in Surface Science and Catalysis*, eds. P. A. Jacobs, N. I. Jaeger, L. Kubelková and B. Wichterlová, Elsevier, Amsterdam, 1991, vol. 69, p. 43.
18 J. W. Ward, in *Zeolite Chemistry and Catalysis, ACS Monograph 171*, ed. J. A. Rabo, American Chemical Society, Washington, 1976, p. 118.

Received in Orsay, France, 5th March 1997;
revised M/S received, 24th October 1997; *Paper* 7/08741A