

# Selective oxidation of benzylic alcohols to aldehydes with metal nitrate reagents catalyzed by BEA zeolites or clays

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The oxidation of benzylic alcohols to benzaldehydes by bismuth(III) nitrate was investigated in the presence of various acidic aluminosilicates. The solid acid was used either as support for the nitrate or simply added in the reaction medium as a catalyst of the decomposition of Bi nitrate. The reactivity of the clay-supported reagent is controlled by the dispersion of the nitrate. A high dispersion requires both high surface area and high acidity of the support. There is a good correlation in the oxidation of benzyl alcohol—as the model reaction—between the structure and the chemical activity of the two main groups of supports (K10 and KSF *vs.* KSF/0 and KP10). In supported reagents made with zeolitic materials such as ZSM-5 or BEA the pores are blocked by the salt, therefore the solvent used for their preparation could not be eliminated completely from the solid. Zeolites cannot, therefore, be used to prepare conventional supported reagents, but work remarkably well, especially BEA, as a catalyst for the oxidation of benzyl alcohol or *m*-phenoxybenzyl alcohol by bismuth nitrate. Similar oxidation results were obtained with iron(III) nitrate.

**Oxydation selective d'alcools benzyliques en aldéhydes par des nitrates métalliques catalysée par des zéolithes BEA ou des argiles.** L'oxydation d'alcools benzyliques en aldéhydes par le nitrate de bismuth a été étudiée en présence de plusieurs aluminosilicates. Les acides solides étaient mis en œuvre soit comme le support du nitrate, soit additionnés simplement au milieu réactionnel comme catalyseur de décomposition du nitrate. La réactivité du réactif supporté par une argile est contrôlée par la dispersion du nitrate. Une bonne dispersion nécessite à la fois une grande surface et une forte acidité du support. Une bonne corrélation existe dans les deux groupes de supports (K10 et KSF *vs.* KSF/0 et KP10) entre structure et activité pour la réaction modèle d'oxydation de l'alcool benzylique. Sur les supports zéolithiques tels que ZSM-5 ou BEA, les pores sont bloqués par le sel ce qui empêche l'élimination du solvant lors de la préparation du réactif supporté. Ces zéolithes ne peuvent donc pas être utilisées pour préparer des réactifs supportés, mais sont d'excellents catalyseurs, surtout la BEA, pour l'oxydation de l'alcool par le nitrate de bismuth. Des résultats similaires ont été obtenus avec le nitrate de fer.

The selective oxidation of alcohols into aldehydes is a simple reaction that is difficult to achieve on the industrial scale, though can be carried out with *tert*-butyl hydroperoxide and Cr-pillared clays.<sup>1</sup> Other solutions have been reported using hydrogen peroxide and titanium zeolites<sup>2</sup> or vanadium silicates<sup>3</sup> or cobalt(II) acetate<sup>4</sup> as catalyst. TS1 gives a high selectivity to aldehyde but the yield is limited to 12–13% since hydrogen peroxide has to be introduced in very small amounts in order to avoid secondary oxidation of the product.<sup>2</sup> This low yield requires huge recycling of the substrate. In the case of vanadium silicate catalysts, the conversions obtained with an excess of H<sub>2</sub>O<sub>2</sub> are limited to <20% at most, whatever the structure of the alcohol.<sup>3</sup> Using cobalt acetate the oxidation of benzyl alcohol leads exclusively to benzaldehyde but the efficiency of H<sub>2</sub>O<sub>2</sub> is poor because a significant amount of oxygen is liberated too.<sup>4</sup>

These yields could be accepted for bulk chemicals but are too low for fine chemistry, and alternative solutions have been proposed based on the use of metallic nitrates, which give high yields and allow eventual leaching of the Cr catalysts to be avoided. The deposition of these nitrates on an appropriate

support allows them to be used as selective, safe and eco-friendly reagents. This process has been described first with acid-treated montmorillonites (for instance K10, KSF from Süd Chemie) and has found industrial applications.<sup>5,6</sup> It can be remarked, however, that the scale-up of supported reactants is difficult. In this process the oxidant is the nitrate ion, according to the detailed mechanism reported by Cornélis and Laszlo,<sup>7</sup> and the preparation of the supported reagent consists basically in the deposition of metallic nitrates onto dealuminated clays using a solution of the salt in acetone, producing clayfen and claycop, for example.<sup>7,8</sup>

It appears, however, that the support is not chemically inert in this process and the physico-chemical characterization of these solids by IR spectroscopy, thermal analysis and X-ray diffraction led to the conclusion that these supported nitrates are in fact hydrated salts,<sup>9</sup> nearly amorphous due to the small size of the crystals. Indeed, the acidic support acted as a catalyst for the decomposition of the nitrate and could be used as a usual catalyst, that is added as a component in the slurry containing the reagents and the nitrates. This catalytic technique, earlier denominated as formation of the reagent *in situ*,

worked remarkably well with several nitrates and clays, these latter being repeatedly used as normal catalysts.<sup>10</sup> The above catalytic technique was applied also for the selective oxidation of the fragile *m*-phenoxybenzyl alcohol to the corresponding aldehyde.<sup>10</sup> Cornélis and Laszlo have pointed out that zeolites cannot be used to make supported reagents.<sup>7</sup> Since zeolites are very common solid acids, it appeared worthwhile to understand the reason for this failure and to investigate their possible application in the catalytic method.

Iron(III) and bismuth(III) nitrate are the most effective among the metal nitrates supported on K10. In the reactions with supported iron(III) nitrate, designated as Fe/K10, a part of the solid remained stuck on the walls of the flask, therefore this reagent was not suitable for more precise evaluation. This problem was not observed with Bi/K10, therefore bismuth(III) nitrate was deposited on different supports and the structure-activity correlation of the individual reagents was investigated in the oxidation of benzylic alcohols for which clayen and claycop were particularly active.<sup>7</sup> Most bismuth compounds are relatively non-toxic, readily available at low cost and are fairly insensitive to small amounts of water.<sup>11</sup> A comparison was made also by the same catalytic systems using several aluminosilicates including ZSM-5 and BEA zeolites. The main difference between zeolites and clays is in the size of the pores: while acid-treated clays are mesoporous (average pore size 4.4 to 7 nm), zeolites are microporous with pore sizes of 0.6 nm for ZSM-5 and about 0.7 nm for BEA.

## Experimental

### Materials

Several members of the K-series from Süd Chemie (Germany) were used as supports or catalysts: KSF, KSF/0, KP10 and K10 while HZSM-5 is an industrial solid from MOL Co. (Hungary). BEA zeolite was prepared according to the procedure of Martens *et al.*<sup>12</sup> with a Si/Al ratio of 7.8. The zeolite was converted to a solid acid (acidity: 0.46 meq g<sup>-1</sup>) by exchange with NH<sub>4</sub>Cl (1 M) cations followed by calcination in oxygen at 350 °C for 3 h. The structure of the supported reagents was characterized by X-ray diffraction and thermal analysis. The characteristics of the zeolite materials and clays are reported in Tables 1 and 2, respectively.

### Preparation of the supported reagents

Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (13.5 g) was added to acetone (187 cm<sup>3</sup>) in a 0.5 L evaporating flask. The mixture was stirred vigorously for 15 min until complete dissolution of the crystals of the hydrated metal nitrate. The clay or zeolite sample (15 g) was added in small amount 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 20 °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

**Table 1** Pore characteristics of zeolites and of supported bismuth nitrate reagents

Sample	Micropore volume/cm <sup>3</sup> g <sup>-1</sup>	
	ZSM-5	BEA
Zeolite	0.115	0.153
Bi/zeolite	0.030	0.021
Bi/zeolite heated to 500 °C	0.064	0.077

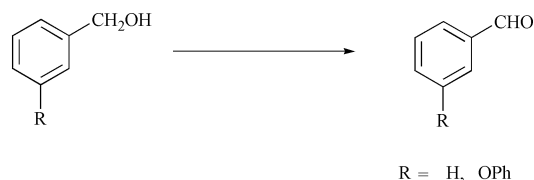
**Table 2** Characteristics of the K clays

Sample	Surface area/m <sup>2</sup> g <sup>-1</sup>	Average pore size/nm	Brønsted acidity/arb. units
K10	229	5.6	0.33
KP10	169	7.1	0.49
KSF	9	5.0	0.59
KSF/0	117	7.4	1.03

continued. The dry precipitate was powdered. The nitrate: support ratio was then 10 mmol nitrate (ion) to 1.8 g support.

### Reaction conditions

The oxidation of benzyl alcohol was used as a model.



It was carried out in a batch reactor and monitored by gas chromatography using a column consisting of Celite impregnated by a mixture of PEG 1500, SE-30 and THEED in a 2 : 2 : 1 ratio.

As a reaction procedure either (a) or (b) was applied: (a) 2.27 g of previously prepared *supported reagent* was added to 1.08 g (1.04 cm<sup>3</sup>, 10 mmol) of alcohol, diluted in 50 cm<sup>3</sup> benzene as solvent, at room temperature, followed by heating to 60 °C as reaction temperature—the molar ratio of NO<sub>3</sub><sup>-</sup> : alcohol = 0.67 : 1, corresponding to the stoichiometry of the reaction; (b) in the *catalytic (in situ)* method, the amounts corresponding to those in method (a) [support 1.2 g, hydrated metal nitrate (1.08 g, 2.22 mmol) and alcohol] were added to the benzene solvent at room temperature. The mixture was then heated to the reaction temperature.

For the oxidation of *m*-phenoxybenzyl alcohol, 2 g (1.74 cm<sup>3</sup>, 10 mmol) alcohol was used under the same conditions. The reaction was monitored by HPLC (C18 reversed phase column, methanol : water = 65 : 35 v/v as eluent, UV detection at 254 nm).

### Structural characterization

TG-DTG-DTA curves were recorded using a MOM OD-2 derivatograph. A 240 mg sample was charged in a platinum crucible. The heating rate was 5 °C min<sup>-1</sup> for the metal nitrates, either pure or supported, and 10 °C min<sup>-1</sup> for the supports, in flowing air atmosphere.

X-Ray powder diffraction patterns were recorded on a HZG-4 type diffractometer, using Cu-K<sub>α</sub> radiation (λ = 1.5405 Å), Ni filtered, with a scan rate of 1° min<sup>-1</sup>.

After a 2 h pretreatment at 300 °C in He flow the surface area and porosity measurements were made by Ar adsorption at -185 °C, following the ASTM D 4222-91 standard.

## Results and discussion

### Comparison of zeolites and clays as supports for solid reagents

Thermoanalytical measurements on the zeolite-supported reagents show, at different temperatures (159 °C for Bi/BEA, 146 °C for Bi/ZSM-5) and in different intensities, a very exothermic peak in the DTA trace (Fig. 1), connected with a weight loss. This effect is so strong in the case of BEA that part of the sample was pushed out of the sample holder. The

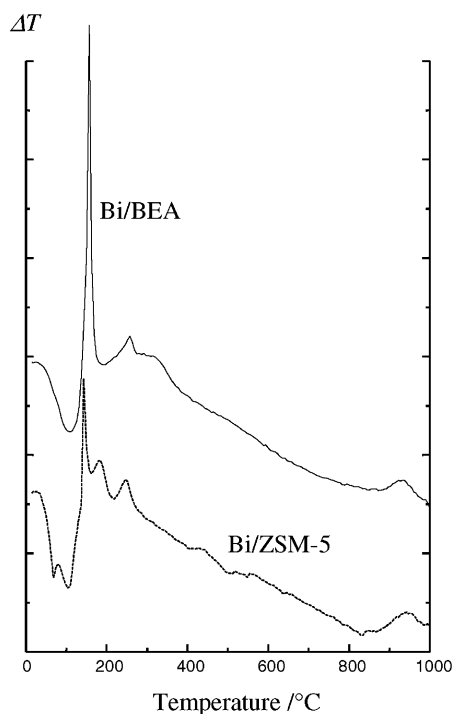


Fig. 1 DTA curves of zeolite-supported bismuth nitrate reagents.

process is reproducible, only its extent can be different. Such a phenomena did not occur with clay-supported reagents (Fig. 2). A reasonable explanation of this difference is that during the preparation the solvent used could not completely evaporate from the zeolite structure because of the blockage of the small pores by solid nitrate. Upon increasing the temperature of the sample, desorption of the residual amount of acetone occurs and the organic material burns on the external surface or is rapidly oxidized by the nitrate. Table 1 clearly shows that the salt impregnated on the zeolite surface fills the pores but after heating up to 500 °C the pore volume is partly regenerated.

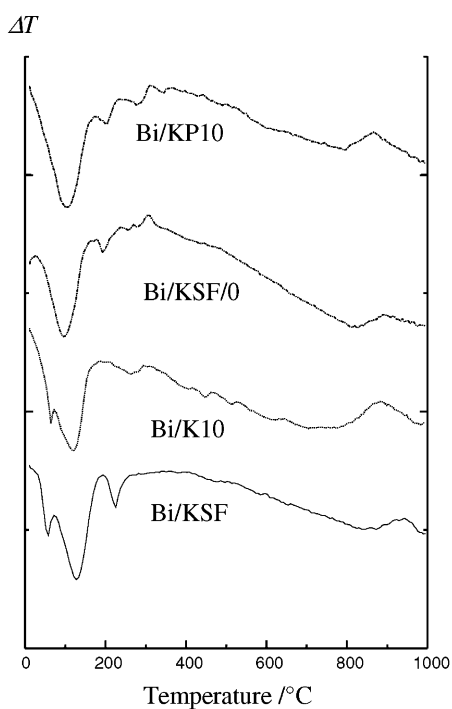


Fig. 2 DTA curves of clay-supported bismuth nitrate reagents.

The K-supported reagents did not show this exothermic decomposition,<sup>9,13</sup> presumably because these solids have a mesoporous structure from which the solvent can evaporate easily and completely during preparation.

The X-ray diffraction patterns of the K-supported reagents show that on K10 and KSF—supports having low specific surface area *or* low Brønsted acidity (Table 2)—bismuth nitrate is present in crystalline form [Fig. 3(a)]. On KSF/0 and KP10, which have higher specific surface area *and* higher Brønsted acidity, bismuth nitrate is present in a modified, partly amorphous phase [Fig. 3(b)]. In this latter case it is possible that part of the metal nitrate has been hydrolyzed as a result of its water of crystallization content and the stronger acidity of the support, producing probably bismuth oxynitrate.

Another difference in the thermoanalytical curves of these two types of K-supported reagents is that the bismuth nitrate on K10 and KSF shows a sharp endothermic peak (Fig. 2) at a temperature (62 and 68 °C, respectively) significantly lower than that of bulk bismuth nitrate (75 °C).<sup>13</sup> This sharp peak has been ascribed to the melting of the nitrate, and the decrease of the melting point was reported in an earlier paper.<sup>13</sup> The reagents supported on KSF/0 and KP10 do not show this endothermic peak probably because some transformation has already occurred as a result of the higher dispersion of the nitrate and the stronger acidity of the support. Moreover, with KSF/0 the decomposition of the metal nitrate has already started: during storage at room temperature a

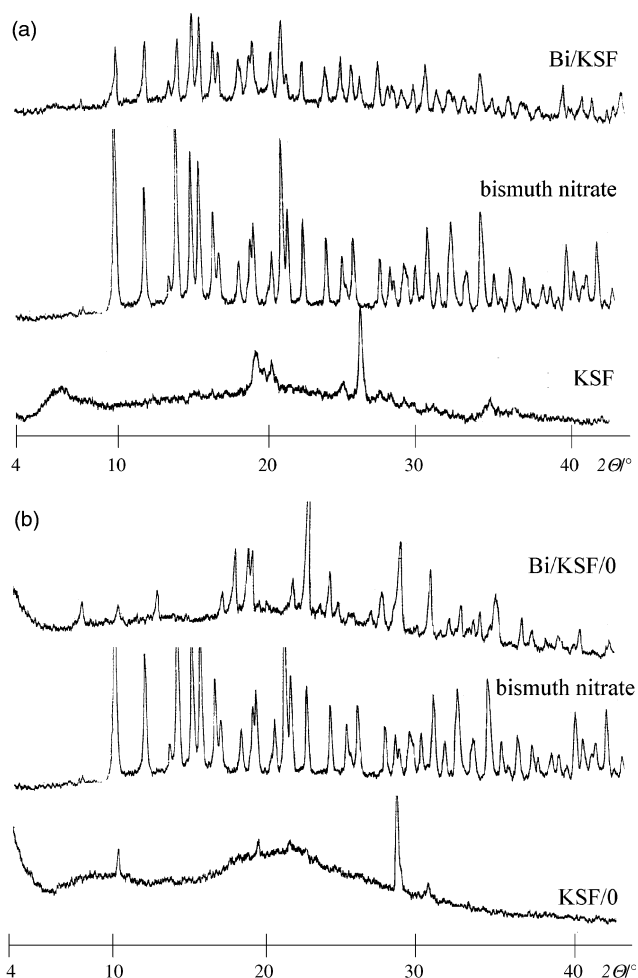


Fig. 3 (a) Comparison of the X-ray diffraction patterns of Bi/KSF supported reagent (top) with those of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (JCPDS-12-148 middle) and the KSF clay (bottom). (b) Comparison of the XRD profile of Bi/KSF/0 supported reagent (top) with the patterns of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (middle) and the KSF/0 support (bottom).

large quantity of nitrous gas was formed. It is interesting to mention that with KSF, also a strong acid, this decomposition does not occur: since this solid shows a much lower specific surface area, this observation suggests that the decomposition occurs at the interface between the nitrate and the support, which is small if the crystals of nitrate are large.

### Oxidation of benzylic alcohols

The two techniques of supported reagent and simple catalysis have been compared using zeolites and clays for the oxidation of benzylic alcohols. With clays both the supported reagents and the catalytic reaction method reach yields above 92%. Table 3 shows clearly that bismuth nitrate alone hardly reacts and solid acids are necessary as catalysts for the oxidation. A good correlation can be found for the mentioned 2 groups of clay materials between structure and chemical activity in the oxidation of benzyl alcohol, with both reaction methods.

Tables 3 and 4 show that with K10 the supported reagent as well as the catalytic system works well and no significant difference is noticed between the two methods. For the KSF-based supported reagent, the initial reaction rate is high but the final conversion is relatively low. In this case the decomposition of the deposited nitrate is very fast and exothermic due to the reaction temperature, therefore the reaction is limited by heat and mass transfer and part of the metal nitrate is decomposed and does not participate in the oxidation. In the catalytic reaction technique the bismuth nitrate species occupy the active sites gradually, the decomposition is much more uniform and the selectivity toward nitrate is better.

In the case of K-supports having the bismuth nitrate in a partly amorphous form, the initial reaction rate with KP10 is higher for the conventionally prepared supported reagent and a strong Brønsted acidity on the support facilitates the nitrate decomposition. With KSF/0 the supported reagent is much less active than the catalytic reaction system, since a large proportion of the bismuth nitrate is decomposed during one

**Table 3** Yields in benzaldehyde (%) obtained in the oxidation of benzyl alcohol with bismuth nitrate, catalyzed by different aluminosilicates (method b)

Solid acid	Reaction time/h					
	0.5	1	1.5	2	2.5	3
None	12	20		20	23	23
K10	—	81	97			
KP10	40	81	92	96	99	
KSF	38	72	86	91	94	99
KSF/0	41	65	77	84	88	92
ZSM-5	13	30	39	48	52	57
BEA	67	74	89	92	97	

**Table 4** Yields in benzaldehyde (%) obtained in the oxidation of benzyl alcohol with conventional supported bismuth nitrate reagents prepared from different supports (method a)

System	Reaction time/h					
	0.5	1	1.5	2	2.5	3
Bi/K10	—	76	85	90	95	
Bi/KP10	51	75	87	92	95	96
Bi/KSF	13	56	71	77	80	81
Bi/KSF/0	3	11	15	19	22	26
Bi/ZSM-5	11	30	46	55	60	64
Bi/BEA	32	67	91	97		

**Table 5** Yields in *m*-phenoxybenzaldehyde (%) obtained in the oxidation of *m*-phenoxybenzyl alcohol with bismuth nitrate, catalyzed by different aluminosilicates

Solid acid	Reaction time/h					
	0.5	1	1.5	2	2.5	3
K10	30	47	65	85	93	
KP10	23	57	81	87	89	
KSF	28	37	66	91		
KSF/0	75	85	94			
ZSM-5	22	43	62	80	87	
BEA	29	63	81	95		

week of storage. In this case the rate of decomposition of the nitrate is much higher than the rate of oxidation of benzyl alcohol.

In the case of zeolites, there is little difference between the performances of the conventional and the catalytic systems. Apparently the residual acetone does not play a significant role in the mechanism, and simply requires more care. There is a clear difference between the activities of the two zeolites: BEA is better than ZSM-5, most probably because of its easier accessibility (larger pore size, very small particles corresponding to a high external surface), and the results with BEA based systems are comparable with those of K10 based systems.

Corresponding to earlier results,<sup>10</sup> *m*-phenoxybenzyl alcohol is well oxidized to aldehyde using different mesoporous clays as catalysts (Table 5) but it is interesting to notice that this rather bulky substrate can be readily and selectively oxidized by also applying the process catalyzed by the microporous BEA. This clearly evidences that the zeolite acts as a catalyst for the decomposition of the nitrate. The zeolite-catalyzed reaction has similar or higher performance than the clay-catalyzed one also in the oxidation of *m*-phenoxybenzyl alcohol. In this case too, BEA has higher activity than ZSM-5. The highest activity of KSF/0 can be explained by the highest acidity and the greatest pore size of this mesoporous material (Table 2).

Similar oxidation results were obtained with iron(III) nitrate, concerning both the differences of the K-catalysts and the applicability of the zeolites.

In conclusion, the catalytic reaction technique is a very useful method for the selective oxidation of benzylic alcohols to aldehydes using metallic nitrates. Since in this procedure the solid acid catalyzes the decomposition of the metallic nitrate, any solid acid can be used; such as strong acid K clays and large pore zeolites like BEA, which gives yields as high as 97% in aldehyde in short times.

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