# Alkylation reactions of potassium carboxylates supported on alumina: comparison between ball-milling, impregnation and dispersion procedures

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Potassium carboxylate alkylation by *n*-bromooctane on neutral alumina in "dry media" under microwave irradiation was studied for different methods of preparation of salt–support powder. Mechanical milling and impregnation techniques led to equivalent yields, much higher than those obtained through dispersion. The first method avoids using solvents and subsequent drying of powders. Crystallographic and granulometric studies of the resulting powders were performed to ascertain the results.

## Introduction

Since the first experiments reported by Keinan and Mazur[1] who studied Nef "dry media" reactions on silica gel, solid supports have been more and more advocated in organic synthesis. They avoid the use of solvents, something which may be advantageous from experimental and environmental points of view. They constitute safe, economical, efficient and eco-friendly conditions in so-called "green chemistry".[2,3] Thus, many anionic alkylations have been performed by using alumina, silica, or clays (such as montmorillonites) as mineral supports. Many studies have then recommended alumina as a very efficient support to carry out organic syntheses.[4–7] Initially, two different techniques were considered, carrying out reactions either by dispersion of the nucleophilic salts onto a mineral support, or by impregnation of the support *via* a saturated solution and subsequent solvent removal under reduced pressure. More generally, though with a very few exceptions,[8] the latter technique (impregnation) is shown to be far more efficient.[9]

More recently, these "dry media" reactions were considerably improved by using microwave (MW) exposure rather than classical heating, thanks to the strong specific interactions of hard-to-heat solid conductors with the electromagnetic field.[10,11] The aim of the present work is to compare the behavior of nucleophilic salts–alumina species with respect to alkylation under MW heating using different modes of preparation: namely dispersion, impregnation, and low-energy ball-milling.

Our reference reaction model[12] was the nucleophilic alkylation reaction of carboxylate anionic species with *n*-bromooctane, reaction (1). The effects of mechanical activation are now well known in inorganic chemistry. Ball-milling

$$\text{RCO}_2^-\text{K}^+ + n\text{-OctBr} \xrightarrow[\text{MW}]{\text{Al}_2\text{O}_3} \text{RCO}_2 n\text{-Oct} + \text{KBr} \quad (1)$$
$$(\text{R} = \text{CH}_3,\ \text{PhCH}_2,\ \text{Ph},\ n\text{-C}_{17}\text{H}_{35})$$

(mechanochemistry), described as a powerful pulverizing and mixing procedure,[13] was recently advocated as a promising technique that could be superimposed on various phenomena. Examples include the amorphization of particles, or the modification of oxidation degrees, or the phase transition of mineral materials (reduction of silver oxide into silver metal, formation of boron nitride and lead dioxide high pressure phases among others). Another important result relates the change of the particle surface area and the size reduction observed for hard and soft materials.[14] Some examples of organic syntheses carried out by means of vibratory mills include: the solid-phase synthesis of a racemic binaphthol,[15] the mechanohydrogenation of naphthalene and biphenyl with alumina and hydrogen,[16] the synthesis of fullerene $C_{60}$, dimer $C_{120}$, achieved by solid-state mechanochemical reaction of $C_{60}$ with KCN or $CH_3COOK$,[17] and the mechanochemical arylation and alkylation of $C_{60}$ under solvent-free conditions.[18]

## Experimental

### Preparation of carboxylate salts

Potassium acetate and benzoate (purchased from Acros) were used without further purification. Potassium stearate and phenylacetate were prepared as usual by dissolving 3.25 g potassium hydroxide (50 mmol containing 15% water) in 50 ml methanol inside an Erlenmeyer flask with stirring. By subsequent addition of carboxylic acid (50 mmol), 14.22 and 6.81 g of stearic and phenylacetic potassium salts were obtained, respectively, after methanol removal and drying to give soft white anhydrous powders. However, due to their hygroscopic character, these materials must be carefully stored. As a matter of fact, X-ray diffraction patterns (XDP) and IR spectra reveal that potassium acetate and phenylacetate quickly absorb water after exposure to ambient atmosphere.[19] Neutral alumina from Merck (activity I, 0.063–0.200 mm, 70–230 mesh ASTM), characterized by small hard grains, was used for these experiments.
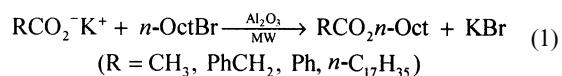
**Table 1** GC analyses of *n*-octyl esters RCOO*n*-C$_8$H$_{17}$

| R | $T$/°C$^a$ | $t_R$/min$^b$ | Standard | $t_R$/min$^b$ |
|---|---|---|---|---|
| CH$_3$ | 85 | 7.6 | *n*-Undecane | 4.5 |
| *n*-C$_{17}$H$_{35}$ | 250 | 7.0 | Bis(2-ethylhexyl)phthalate | 4.4 |
| Ph | 190 | 3.3 | Di-*n*-butyl phthalate | 4.7 |
| PhCH$_2$ | 170 | 5.8 | *n*-Octyl benzoate | 5.1 |

$^a$ Isothermal oven temperature. $^b$ Retention time.

### Preparation of salt–alumina mixtures

For salt–alumina preparations, three procedures were tested.

**i) *Dispersion* mode (D).** This consists of a simple contact between potassium carboxylate (1 g) and alumina (4 g). The two powders are shaken together vigorously for 5 min in a stoppered flask, with no further treatment.

**ii) *Impregnation* mode (I).** This involves dissolving at room temperature potassium carboxylate (1 g) either in methanol or in water (20 mL), with magnetic stirring, then addition of alumina (4 g). The solvent is subsequently removed under reduced pressure and the supported reagent dried under vacuum.

**iii) *Mechanical milling* mode (M).** This involves a mixture of potassium salt (1 g) and alumina (4 g) put inside a cylindrical steel container and shaken together with 20 metallic balls (about 2 g each). After 4 to 48 h, it was observed that the balls and the lower part of the cylinder inner walls were coated with a thick and hard layer of the inorganic materials, which indicates that the compactness of the powders had been increased. Moreover, part of the powder was often deposited all along the cylinder inner walls, and even on the screw top (*i.e.*, 8 cm above the upper level of the mixture); a dust cloud could be observed on opening the container. This indicates that very small light particles were formed during the course of milling. For potassium stearate, the grains are only flattened at the bottom of the container. We must also stress that, even after shaking for a long time, almost no temperature increase of the containers could be observed, and that the 20 balls induce an apparently negligible pressure.

### Alkylation reaction procedure

Subsequently, using the three types of preparation for the reactant, the alkylation reactions were performed by means of a monomode microwave (Prolabo Synthewave 402, operating at 2.45 GHz).[11,20] In all cases, 5 g of powder and 1.5 molar equivalents of *n*-bromooctane were firmly homogenized inside a glass or quartz test-tube for each treatment.[20] The mixtures were then exposed to MW for 10 min (180–300 W). The temperature *versus* time variation was detected by means of an IR pyrometer and monitored by a computer.[20,21] After cooling down to room temperature, the mixtures were eluted with diethyl ether (50 mL) by filtering through sintered-glass. The filtrates were analyzed by gas chromatography (GC) with an internal standard using a Carlo Erba apparatus [Vega series 2 GC 6000 flame ionization, capillary column CPSil 5 CB (25 m), gas carrier: Ar (70 kPa), injector-detector temperature: 280 °C]. For every salt, oven temperatures, retention times, and internal standards are indicated in Table 1.

### Particle analysis techniques

Grain size analyses were carried out by means of a Mastersizer micro (Malvern Cy) granulometer. Surface area measurements were performed with a Sorptomatic 1900 apparatus (Carlo Erba Cy). The results were obtained after nitrogen adsorption according to the Brunauer–Emmett–Teller (BET) method. The powders were previously maintained under a low vacuum

**Table 2** *n*-Octyl ester yields [reaction (1)] after 10 min 180 W MW irradiation for different RCOO$^-$K$^+$–alumina preparation techniques

| R | Procedures | MW final $T$/°C | Yield (%) |
|---|---|---|---|
| CH$_3$ | D | 185 | 49 |
| | I (*via* H$_2$O) | 203 | 80 |
| | I (*via* MeOH) | 200 | 60 |
| | M (8 h) | 185 | 75 |
| | M (20 h) | 186 | 79$^a$ |
| *n*-C$_{17}$H$_{35}$ | D | 155 | 32 |
| | I (*via* MeOH) | 185 | 35 |
| | M (8 h) | 156 | 22 |
| | M (20 h) | 197 | 30$^a$ |
| Ph | D | 182 | 0 |
| | I (*via* H$_2$O) | 170 | 34 |
| | I (*via* MeOH) | 179 | 7 |
| | M (8 h) | 184 | 11 |
| | M (20 h) | 200 | 34$^a$ |
| PhCH$_2$ | D | 172 | 67 |
| | I (*via* H$_2$O) | 169 | 76 |
| | I (*via* MeOH) | 168 | 65 |
| | M (4 h) | 204 | 60 |
| | M (8 h) | 206 | 68$^a$ |

$^a$ Prolongated exposure to MW does not give improved yields.

$(3 \times 10^{-2}$ Torr) at ambient temperature. Scanning electron microscopy (SEM) was used to observe the particles. The crystalline unit-cells were determined by X-ray diffraction (Guinier-de Wolff Camera II, Enraf-Nonius apparatus, fitted with a quartz monochromator).

## Results

### Alkylation reactions

The ester yields obtained for the three methods, D, I and M, are listed in Table 2. The reactions were performed under the same experimental conditions (10 min 180 W microwave exposure).

No general rule can be drawn as to what affects the relative yields for the three methods. For method I, it appears that impregnation from water leads to yields improved by 10 to 25% relative to those obtained *via* methanol (except for potassium stearate, which is insoluble in water). This could be due to the part played by small amounts of water in the reaction. The role of water has been demonstrated for some substitution reactions performed in "dry media",[22] or under solid–liquid phase transfer catalysis.[23] Traces of water are shown to induce some dissociation of the nucleophilic salts as RCOO$^-$K$^+$ and thus to diminish lattice energies.

Concerning mode M, after ball-milling for 8 h, yields exceed by 5 to 25% those obtained after 4 h. Mode D leads to yields nearly equivalent to those by the I and M methods for potassium stearate and phenylacetate, a lower yield (10 to 30%) for potassium acetate, and a nil yield for potassium benzoate. Finally, the I and M methods lead to higher, almost equivalent yields.

Three complementary experiments with potassium phenylacetate were also performed to optimize procedure M. The salt and alumina were either shaken separately or not shaken at all. Whatever the treatment of the salt powder was, the alkylation procedure led to yields close to those given in Table 2 (60%) after the alumina powder had been shaken alone. However, this yield is somewhat lower for non-shaken alumina (54%). So, it appears that, after grinding, alumina enhances slightly the alkylation yield.

The alkylation reaction was tentatively performed by using α-Al$_2$O$_3$ (corindon) instead of η-Al$_2$O$_3$. After mixing with the salt, then ball-milling for 48 h, the powder was reacted for 10 min under MW at 175 °C. The final yield was equal to 8%. The presence of corindon (or possibly of another alumina form, or aluminium trihydroxide) would seem to have a noticeable effect on the final yield.
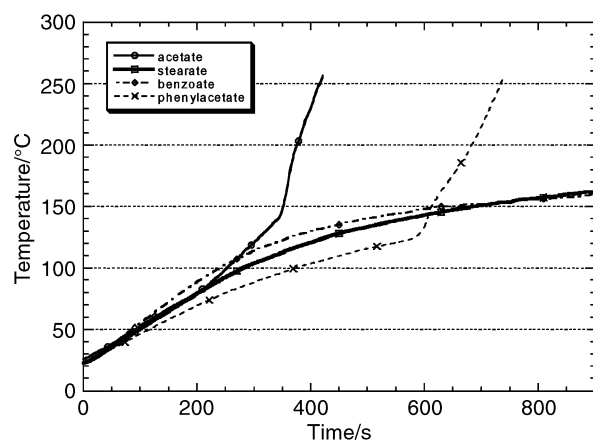
**Fig. 1** Thermal evolution of ball-milled potassium carboxylates–alumina when submitted to MW exposure ($P = 180$ W).
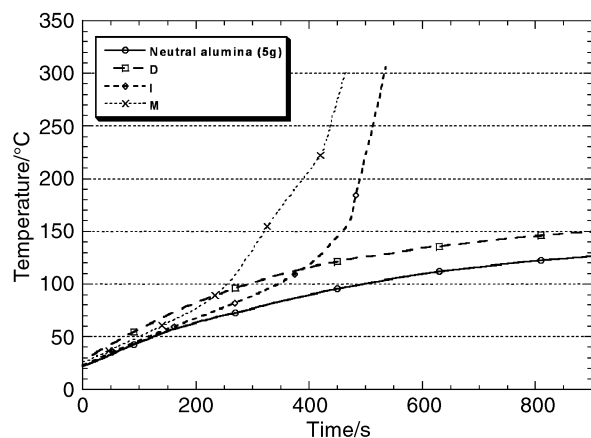


**Fig. 2** Thermal evolution of potassium acetate–alumina (1 : 4 w/w) when submitted to MW exposure ($P = 300$ W) according to different preparation procedures (D = dispersion, I = impregnation, M = ball-milling).

### Thermal behaviors of the different preparations when submitted to MW exposure

The profiles of temperature raising of samples when submitted to MW exposure[12b] are correlated with their polarization: the more polar the medium, the more important the temperature increase.

In Fig. 1, the thermal behaviors of various carboxylates, ball-milled on alumina, are compared.

With potassium acetate and phenylacetate, these variations are characterized by a thermal runaway that reveals a high degree of ionic dissociation of these compounds when ball-milled on alumina. For the stearate and benzoate salts, the temperature tends towards a plateau (160 °C). Thus polarity effects increase according to the following sequence: acetate > phenylacetate > benzoate ≈ stearate.

This order is the same as for the reactivity (Table 2) when one considers the yields of the reaction with *n*-bromooctane. Different $CH_3COO^-K^+$–alumina preparations are compared in Fig. 2.

Ball-milled and impregnated reactants exhibit obviously the same behaviors, with a thermal runaway after short MW exposures (5–6 minutes). The temperature in dispersed samples remains moderate and tends towards a plateau. Thus, the ionic dissociation of $RCOO^-K^+$, and consequently its polarity increase, is in the order: impregnation ≈ ball-milling > dispersion.

This sequence is the same as that reported for reactivity (Table 2). These thermal behaviors are therefore strictly connected to the observed reactivities as involving a more or less

**Table 3** Granulometry, surface areas and $c$ (BET) parameter for the different samples

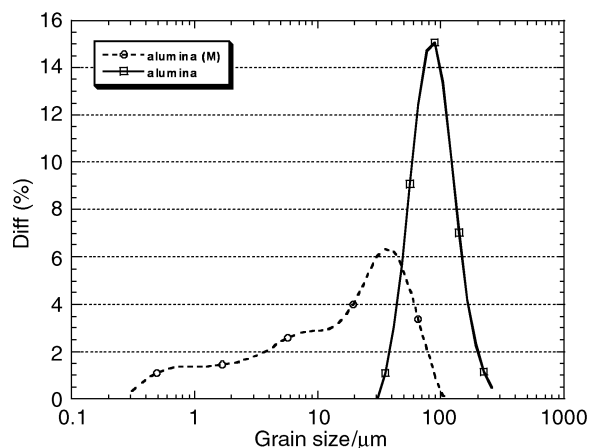| Samples | Granulometry $D$ (v, 0.5)/mm | Surface area BET/ $m^2 g^{-1}$ | $c$ | Alkylation yield (%) |
|---|---|---|---|---|
| $Al_2O_3$ | 92 | 132 | $102 \pm 2$ | — |
| $Al_2O_3$ (M) | 19 | 126 | $103 \pm 2$ | — |
| AcOK | 159 | 0 | | 0 |
| AcOK (M) | 86 | 0 | 0 | — |
| (AcOK + $Al_2O_3$) (D) | 97 | 80 | $48 \pm 1$ | 49 |
| (AcOK + $Al_2O_3$) (M) | 7 | 40 | $30 \pm 1$ | 75 |
| AcOK–$Al_2O_3$ (I) (*via* $H_2O$) | 103 | 22 | $54 \pm 4$ | 80 |



**Fig. 3** Granulometry of alumina before and after ball-milling.

important ionic dissociation of $RCOO^-K^+$ due to alumina interaction.

### Granulometry, geometric and surface areas

Powders of alumina, potassium acetate and of potassium acetate–alumina mixture were studied with respect to their grain sizes [measured as $D$ (v, 0.5) (medium diameter particles)], and their surface areas were measured according to the BET method (nitrogen adsorption). In the case of a pure AcOK powder, the lack of adsorption of nitrogen is due either to the very low surface area, or to the fact that a part of the particles are readily saturated by water. The results reported in Table 3 allow us to correlate these values with the alkylation yields.

1) For granulometry measurements, alumina powder (before and after ball-milling) is readily suspended in water. To avoid potassium acetate solubilization in water and the formation of aggregates, pure acetate and alumina–acetate mixtures were dipped into a benzine gas–oil mixture (ratio 50 : 50). Grain size changes after treatments M and D are shown on Fig. 3 (alumina), Fig. 4 (potassium acetate) and Fig. 5 (potassium acetate–alumina). Note that, after treatment M: a) the formation of new populations with smaller diameters is obvious (Figs. 3 to 5); b) the medium grain diameter is thus reduced by a ratio of about 2 (acetate) and 5 (alumina) (Table 3); c) the amount of submicronic grains is noteworthy (Figs. 3 and 5).

However, it would be difficult to wash off the AcOK–alumina mixture without inducing unwanted reactions. Indeed, only water can be used to dissolve the carboxylate, and this could lead either to the formation of alumina hydroxide at the grain surfaces, or to that of the AcOK hydrated phase after drying.[19]

2) BET measurements were performed to determine the surface areas and the $c$ parameters. Unfortunately, it was not possible to calculate the t-plot values. Indeed, the standard curve for a non-porous oxide was not recorded under the same
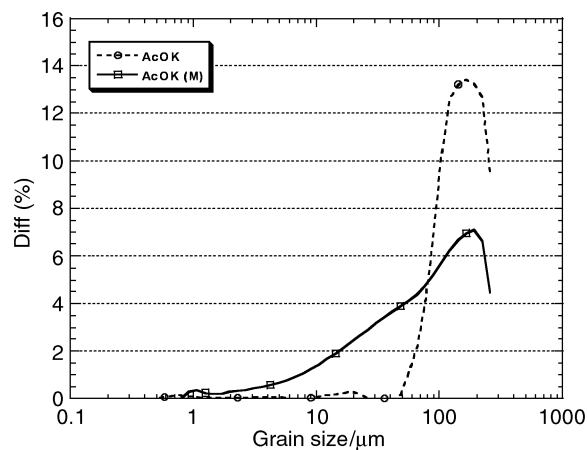
**Fig. 4** Granulometry of potassium acetate before and after ball-milling.
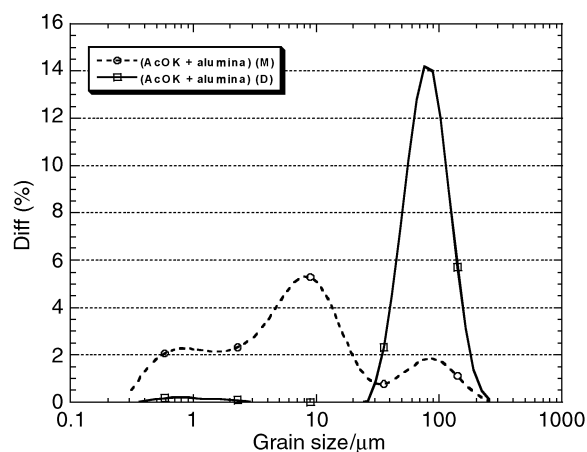


**Fig. 5** Granulometry of ball-milled and dispersed potassium acetate–alumina systems.



**Fig. 6** Scanning electron microscopy (SEM) imaging of alumina powder: a) before ball-milling; b) after ball-milling.

experimental conditions as those used for our samples. Adsorption/desorption isotherm curves show an hysteresis and can be classified as type IV.[24] The BET plot is linear with the origin at 0, or very close to 0. Such curves allow us to qualify the materials as mesoporous.

The results given in Table 3 clearly show the following. a) Surface area of alumina is weakly affected by ball-milling; this could be due to the increase in the external surface (see Figs. 6a and 6b) and a decrease in the mesoporosity observed after pressure treatment. b) Potassium acetate does not adsorb nitrogen; this is related either to the presence of water inside numerous pores, or to the low surface area of the particles. c) Surface areas decrease from dispersed to ball-milled and finally to impregnated samples, whereas the $c$ parameter, relative to that for alumina, drops by a factor of 2 after treatments D and I, and by a factor of 3 after treatment M (the $c$ parameter is exponentially related to the surface energy).

As we could not perform microcalorimetry experiments, it is difficult to draw conclusions about the activation processes and consequent alkylation yield changes. In fact, these data seem to be related to the parameter changes as reported in Table 3, to the particle aspects as seen in Figs. 6 to 9, and to MW heating (Fig. 1). For instance, the decrease of surface area after treatments M and I could be linked either to site coverage (sticking of small potassium salt particles on alumina grains), or to micropore filling (therefore a loss of microporosity). The high alkylation yields after ball-milling could be due to the large amount of very small crystallites and to the larger apparent surface of the aggregates. This could balance the lower surface
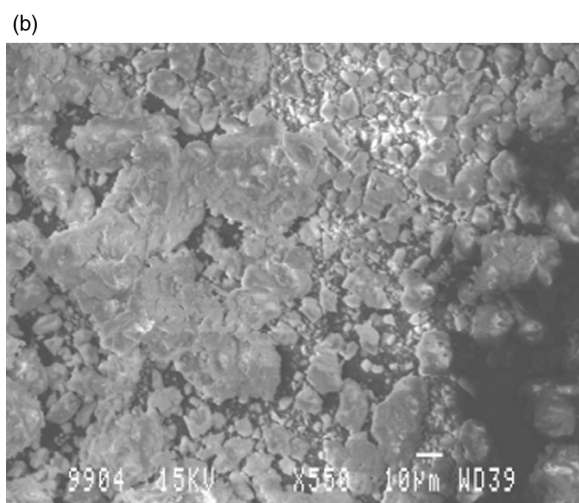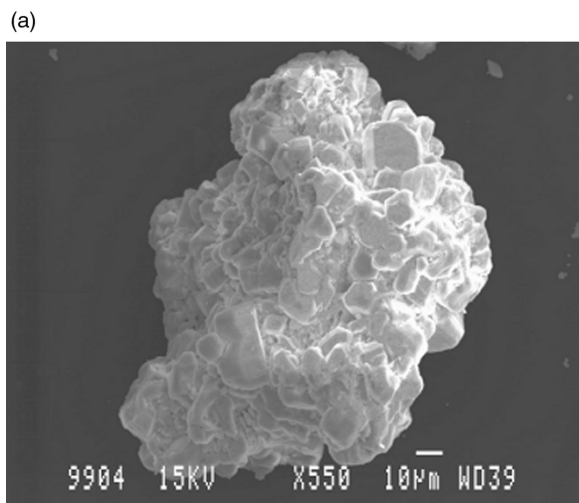
energy recorded for this material. So far, we cannot make any conclusions about the activation modes for the different procedures, particularly as the possible presence of water could play a non-negligible role (as a catalyst) during and after the treatments D, I and M.

**Particle imaging**

In order to check the above hypothesis, SEM imaging was carried out.

**a) Alumina.** SEM imaging shows that the initial powder is made of polygonal crystallites of various sizes (Fig. 6a). After grinding, these crystallites are smaller, thinner, and exhibit large apparent surfaces (Fig. 6b). Such a configuration can enhance interfacial contacts with grains of another very fine powder.

**b) Potassium acetate.** For a non-milled potassium acetate powder, the initial small crystallites appear as spherolites or rounded shapeless volumes with sizes higher than 300 µm.[19] After grinding, these spheres and volumes are smaller (50–200 µm), many grains exhibit polygonal shapes, and others are characterized by very small sizes (less than 5 µm) (Fig. 7a and b).

**c) Potassium acetate–alumina.** When alumina and potassium acetate powders are ball-milled together, SEM imaging shows large shapeless aggregates, with many submicronic particles sticking to their surfaces (Fig. 8). This can be understood in
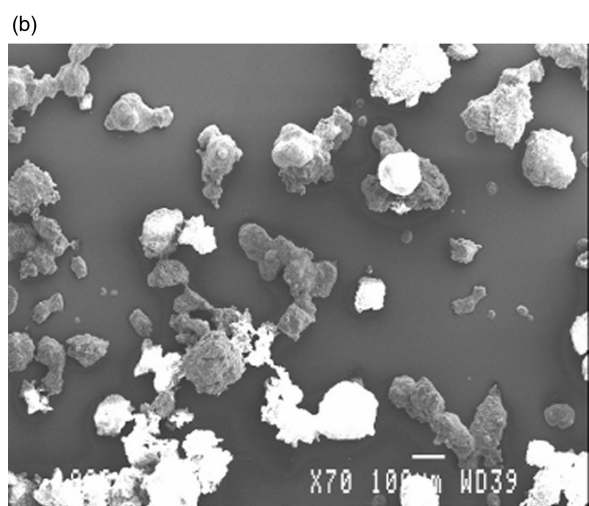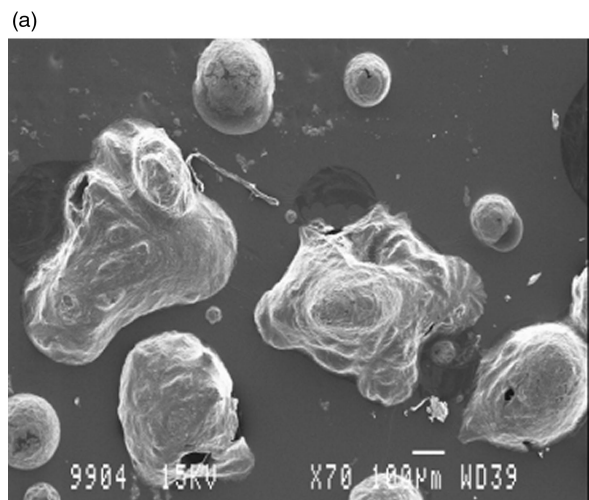
**Fig. 7** Scanning electron microscopy (SEM) imaging of potassium acetate powder: a) before ball-milling; b) after ball-milling.
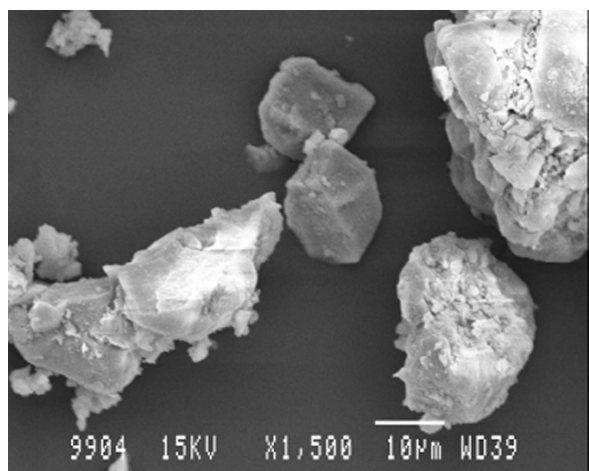


**Fig. 8** Scanning electron microscopy (SEM) imaging of ball-milled alumina–potassium acetate mixture powders.

terms of small potassium acetate crystals sticking onto bigger alumina ones, thus diminishing surfaces able to adsorb nitrogen.

**d) Potassium benzoate.** In the case of potassium benzoate, the initial powders are made of large aggregates (50 to 250 μm). After grinding, they appear flattened and smoothed and some particles have been pulled out and are isolated from one another (Fig. 9a and b). Such a configuration seems to increase efficiently the interfacial contact with alumina.
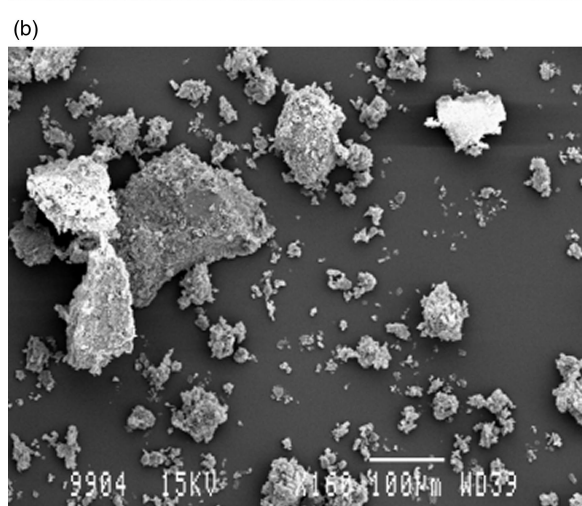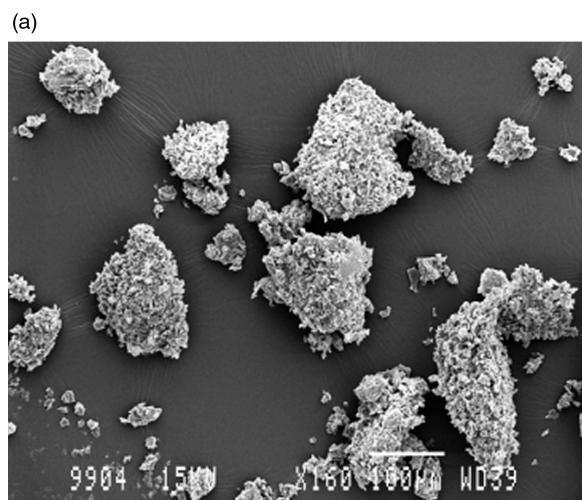


**Fig. 9** Scanning electron microscopy (SEM) imaging of potassium benzoate powder: a) before ball-milling; b) after ball-milling.

**Crystallographic data**

**a) Alumina.** As revealed by XDP, commercial alumina ($\eta$-Al$_2$O$_3$, fcc, a$_F$ = 0.795 nm) is poorly crystallized.[25] Indeed, the patterns exhibit only the presence of a faint and diffuse halo, corresponding to the (440) diffraction line. During ball-milling (ambient atmosphere) and MW exposure (maximum temperature: 130 °C), no phase transition was induced.

**b) Potassium salts.** Crystallographic data concerning potassium salts are somewhat intricate. It has been previously established that commercial potassium acetate is a mixture of hydrated and unhydrated salts. Moreover, under MW exposure, a phase transition occurs near 130 °C.[19] It has been demonstrated that potassium phenylacetate is very sensitive to water; the dry powder can absorb one molecule of water per potassium phenylacetate molecule in less than 30 min. The two other salts are less contaminated by water. IR spectra support these observations.[26] As revealed by XDP, the neat powders used before treatment are well crystallized. After mixture with alumina according to procedures I and M, potassium acetate, phenylacetate and stearate become amorphous. In the case of potassium benzoate, only the most intense peaks are observed as faint diffraction lines; they are more intense after procedure I. It is difficult to determine the unit-cell parameters for potassium benzoate and phenylacetate.

## Conclusion

Our experiments have allowed us to point out the behavior of four potassium carboxylates during alkylation reactions on

alumina by *n*-bromooctane. From our results it appears that potassium stearate and benzoate give the worst yields, and that the dispersion procedure is the least suitable to obtain high reactivities. Potassium acetate and phenylacetate give better yields, overall, after ball-milling and impregnation procedures. To explain such phenomena one can put forward various hypotheses. First, it appears that for potassium acetate and phenylacetate water may play a role, as a catalyst, during the reaction. Second, the size and nature of pores and of defects might also be very important parameters. Particularly, the process M could induce high-activity defect sites. Isotherm curves indicate the mesoporous character of the particles. Unfortunately, SEM observations do not allow us to obtain a sufficient resolution to observe objects smaller than 100 nm. Process M might also induce a better contact between the salt and alumina grains by increasing the external surfaces, and it involves a crystalline⟶amorphous transition (except for potassium benzoate) which should favor salt reactivity. Lastly, one must add that MW treatments depict yields and salt reactivities as a function of the three different procedures. Indeed, thermal runaways are recorded for potassium acetate and phenylacetate and, after I and M procedures, for potassium acetate–alumina mixtures.

Procedure M constitutes a significant simplification of the overall reaction as there is no need for prior impregnation of salts on solid supports and subsequent (often tedious) drying under vacuum. Note that processes I and M last equivalent times (8–20 hours). Moreover, as simple dispersion is not usually sufficient to promote any activation of carboxylate salts, ball-milling (low-energy mechanochemistry) is as efficient as impregnating reagents. Therefore, associated with MW treatment and solvent elimination, procedure M appears very economic and non-polluting. It is a new efficient procedure to obtain satisfactory alkylation yields.

## References

1 E. Keinan and Y. Mazur, *J. Am. Chem. Soc.*, 1977, **99**, 3861.
2 G. Bram and A. Loupy, in *Preparative Chemistry Using Supporting Reagents*, ed. P. Laszlo, Academic Press, New York, 1987, ch. 20, pp. 387–400.
3 J. H. Clark, K. Martin, A. J. Teasdale and S. J. Barlow, *J. Chem. Soc., Chem. Commun.*, 1995, 2037.
4 G. H. Posner, *Angew. Chem., Int. Ed. Eng.*, 1978, **17**, 487.
5 A. McKillop and D. W. Young, *Synthesis*, 1979, 401; A. McKillop and D. W. Young, *Synthesis*, 1979, 481.
6 A. Foucaud, G. Bram and A. Loupy, in *Preparative Chemistry Using Supporting Reagents*, ed. P. Laszlo, Academic Press, New York, 1987, ch. 17, pp. 317–341.
7 G. W. Kabalka and R. M. Pagni, *Tetrahedron*, 1997, **53**, 7999 and references therein.
8 (*a*) J. Barry, G. Bram, G. Decodts, A. Loupy, P. Pigeon and J. Sansoulet, *Tetrahedron*, 1983, **39**, 2669; (*b*) E. R. Perez, A. L. Marrero, R. Perez and M. A. Autié, *Tetrahedron Lett.*, 1995, **36**, 1779.
9 (*a*) S. L. Regen, S. Quici and S. J. Liaw, *J. Org. Chem.*, 1979, **44**, 2029; (*b*) J. Barry, G. Bram, G. Decodts, A. Loupy, P. Pigeon and J. Sansoulet, *Tetrahedron*, 1983, **39**, 2673.
10 G. Bram, A. Loupy and D. Villemin, in *Solid Supports and Catalysts in Organic Chemistry*, ed. K. Smith, Ellis Horwood PTR Prentice Hall, Chichester, 1992, ch. 12, pp. 301–326.
11 A. Loupy, A. Petit, J. Hamelin, F. Texier-Boullet, P. Jacquault and D. Mathé, *Synthesis*, 1998, 1213.
12 (*a*) G. Bram, A. Loupy, M. Majdoub, E. Guttierez and E. Ruiz-Hitzky, *Tetrahedron*, 1990, **46**, 5167; (*b*) A. Loupy, P. Pigeon and M. Ramdani, *Tetrahedron*, 1996, **52**, 6705.
13 (*a*) V. V. Boldyrev, *J. Chim. Phys. (Paris)*, 1986, **83**, 821; (*b*) P. Yu Butyagin, *Russ. Chem. Rev.*, 1994, **63**, 965; (*c*) J. F. Fernandez-Bertran, *Pure Appl. Chem.*, 1999, **71**, 581.
14 (*a*) H. Szwarc and M. Gasgnier, *J. Solid State Chem.*, 1998, **136**, 51; (*b*) M. Gasgnier and H. Szwarc, *J. Mater. Sci.*, 2000, **35**, 3003.
15 M. O. Rasmussen, O. Axelsson and D. Tanner, *Synth. Commun.*, 1997, **27**, 4027.
16 L. D. Field, S. Sternhell and H. V. Wilton, *Tetrahedron Lett.*, 1998, **39**, 115.
17 K. Komatsu, G. W. Wang, Y. Murata, T. Tanaka, K. Fujiwara, K. Yamamoto and M. Saunders, *J. Org. Chem.*, 1998, **63**, 9358.
18 T. Tanaka and K. Komatsu, *Synth. Commun.*, 1999, **29**, 4397.
19 M. Gasgnier and A. Petit, *J. Mater. Sci.*, 1994, **29**, 6479.
20 (*a*) R. Commarmot, R. Didenot and J. F. Gardais, French Patent 2 560 529 (1985); Rhône-Poulenc/Prolabo, *Chem. Abstr.*, 1986, **105**, 17 442; (*b*) P. Jacquault (Prolabo Company), European Patent 545 995 AI (21.12.1992).
21 (*a*) M. Gasgnier, A. Loupy, A. Petit and H. Jullien, *J. Alloys Compd.*, 1994, **204**, 179; (*b*) M. Gasgnier, A. Petit, H. Jullien and A. Loupy, *Mater. Res. Bull.*, 1996, **31**, 1101.
22 (*a*) T. Ando, T. Kawate, J. Yamawaki and T. Hanafusa, *Chem. Lett.*, 1982, 935; (*b*) T. Ando, T. Kawate, J. Yamawaki and T. Hanafusa, *Chem. Lett.*, 1984, 725.
23 (*a*) H. A. Zahalka and Y. Sasson, *J. Chem. Soc., Chem. Commun.*, 1984, 1652; (*b*) S. Dermeik and Y. Sasson, *J. Org. Chem.*, 1985, **50**, 879; (*c*) G. Bram, A. Loupy and M. Pedoussaut, *Tetrahedron Lett.*, 1986, **27**, 4171.
24 S. J. Gregg and K. S. W. Sing, in *Adsorption, Surface Area and Porosity*, Academic Press, New York, 1982, p. 4.
25 H. C. Stumpf, A. S. Russell, J. W. Newcombe and C. M. Tucker, *Ind. Eng. Chem.*, 1950, **42**, 1398.
26 M. Gasgnier, *J. Mater. Sci. Lett.*, in the press.