Synthesis of Layered Disodium (or Dipotassium) *Tetrakis*-(octanoate-o)-Zinc(II) and Preliminary Investigation of the Catalytic Activity in the Esterification of Octanoic Acid with Isopropanol¹

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Received August 21, 2016

Abstract—This paper reports the synthesis of layered zinc/sodium and zinc/potassium octanoates $(A_2[Zn(C_8H_{15}O_2)_4], A = Na^+ \text{ or } K^+)$, two underexplored carboxylates, through reaction of the octanoate of the desired alkali metal with a zinc salt. After drying and chemical characterization, their catalytic activities were tested in the esterification of octanoic acid with isopropanol. Conversion values were high for the reactions conducted under following conditions: temperature 155°C, isopropanol/octanoic acid molar ratio = 8 : 1, catalyst/octanoic acid ratio 7 wt %, and reaction time 2 h. Isolation of the catalysts after esterification showed that the materials were converted into zinc octanoate in situ.

Keywords: zinc/sodium and zinc/potassium octanoates, esterification, octanoic acid, conversion in esterification

DOI: 10.1134/S0023158417060076

INTRODUCTION

Alkanoates or metal carboxylates (metallic soaps) combine anions derived from fatty acids with metals in various oxidation states and have the generic formula $(C_nH_{2n + 1}COO^-)_xM^{x+}$, where M^{x+} corresponds to a metal with oxidation state x^+ , with *x* ranging from 1 to 3 [1, 2]. These compounds have wide industrial applications including their use as polymers, components of paints with hydrophobic properties, thickener of lubricating greases, lubricants employed in various industrial branches, and liquid crystals [3, 4].

More recently, layered carboxylates containing metals in the oxidation state 2+, especially Zn^{2+} , have proven to be active catalysts during the esterification of fatty acids with alcohols of different chain sizes [5-8]. This class of catalysts has many advantages: they can be added to the reaction medium in the solid state, they are solubilized/merged during the reaction, and they are recovered intact after reaction cooling. Therefore, layered carboxylates offer the best advantages of both heterogeneous and homogeneous catalysts.

Although the main goal of research into esterification reactions is to obtain fatty esters for biodiesel purposes, esterification can also afford other valuable esters such as isopropyl octanoate produced by reacting octanoic acid with isopropanol [9].

Considering that the structures of carboxylates involving alkali metals and Zn^{2+} ions have been described in the literature [10, 11], and that these compounds were identified in paints used in works of art [7], this study is aimed at evaluating this class of materials as alternative, highly active catalysts for the production of isopropyl octanoate from octanoic acid and isopropanol. It is noteworthy that to date neither $Na_2[Zn(C_8H_{15}O_2)_4]$ nor $K_2[Zn(C_8H_{15}O_2)_4]$ were used in other applications.

EXPERIMENTAL

Layered disodium (or dipotassium) *tetrakis*-(octanoate-O)-zinc(II) $(A_2[Zn(C_8H_{15}O_2)_4]$, designated $A_2[Zn(B)_4]$ hereafter (where A corresponds to Na⁺ or K⁺ and B refers to the anion octanoate $(C_8H_{15}O_2^-)$) and denoted zinc/sodium (or zinc/potassium) octanoates, were synthesized according to the procedure adapted from the literature on the synthesis of zinc/sodium (or zinc/potassium) hexanoates [10, 11].

Sodium or potassium octanoates were produced by reacting octanoic acid (120.3 mmol) solubilized in methanol (40 mL) with methanolic NaOH or KOH solutions taken in stoichiometric amounts and pre-

¹ The article is published in the original.



Fig. 1. X-ray diffraction patterns (a) and FTIR spectra (b) of zinc/sodium octanoate (*1*) and zinc/potassium octanoate (*2*).

pared in advance at 50°C under vigorous stirring. The resulting sodium octanoate precipitate was solubilized in 50 mL of distilled water at room temperature under magnetic stirring.

Zinc/sodium (or potassium) octanoates were synthesized by slow adding an anhydrous zinc chloride (98%) solution containing 60.15 mmol of the zinc salt in 100 mL of distilled water to the solution containing sodium (or potassium) octanoate, under magnetic stirring. After zinc chloride was added, the mixture was stirred for 30 min. The resulting white solid was washed with distilled water and centrifuged twice followed by drying in a vacuum oven at 60°C to a constant weight.

The catalytic activity assays were restricted to the synthesis of isopropyl octanoate, an aliphatic ester that is used as food flavoring and is difficult to synthe-

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size. In the industry, this ester is obtained with low yields and high market value. In the experiments, octanoic acid (98%) and isopropanol (98%) were placed in a BüchiGlasUster reactor miniclave driven with rotation of 500 rpm and connected to a Julabo HE-4 oil bath. Based on previous tests, 500 rpm was chosen as the ideal stirring rate in order to ensure a potential impact of mass transfer, and because higher stirring rates (750 rpm, 1000 rpm, etc.) did not lead to a significant increase in the acid-ester conversion. The reaction conditions: alcohol/acid molar ratio = 8 : 1, catalyst/octanoic acid ratio = 7 wt %, temperature 155°C, and reaction time 2 h. Acid conversion into the ester was quantified by titration of the resulting mixture with NaOH 0.1 mol/L previously standardized with potassium biphthalate.

X-ray powder diffraction (XPRD) patterns of all samples were recorded on a Shimadzu XDR-6000 diffractometer using Cu K_{α} radiation ($\lambda = 1.5418$ Å), at 40 keV, 30 mA, and a scanning rate of 2°/min. The samples were placed on glass sample holders and lightly hand pressed so that the crystals were perfectly set in the holder plane.

Fourier-transform infrared spectroscopic measurements (FTIR) were conducted by using the samples pressed as KBr discs (spectroscopic grade, Vetec). The spectra were acquired on a Bio-Rad FTS 3500GX spectrophotometer between 400 and 4000 cm⁻¹, with a resolution of 4 cm⁻¹ and accumulation of 32 scans.

Thermal analysis measurements (simultaneous thermogravimetry, TGA, and differential scanning calorimetry, DSC) were performed on a Netzsch STA 449 F3 Jupiter analyzer under the following conditions: synthetic air flow 50 mL/min, heating rate 10°C/min, and temperature ranging from 30 to 1000°C. The samples were placed in alumina crucibles.

Energy dispersive spectroscopy (EDS) was accomplished with the aid of a microscope VEGA3 Tescan LMU (EDS-Oxiford) equipped with the AZ Tech (Advanced) software, an 80 mm² SDD detector, and voltage of 15 kV. Powder samples were placed in the sample holder and fixed with commercial glue. The scans were collected from 0 to 11 keV. After EDS analysis, the samples were metal sputtered, and micrographs were obtained by scanning electron microscopy (SEM) under the same microscope.

High-resolution DSC analyses were carried out on a Netzsch 200F3 calorimeter with the samples placed in aluminum crucibles. The conditions were as follows: N₂ flow 20 mL/min, heating rate 10°C/min, and temperature ranging from 20 to 160°C.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of zinc/sodium octanoate and zinc/potassium octanoate (Fig. 1a) are typical of layered materials: a series of diffraction peaks emerge at low angles.

To avoid errors associated with low angle diffraction peak positions, the interplanar spacing was determined from the peak positions at higher Bragg angles. Unit cell dimensions of 23.94 and 20.77 Å characterize zinc/sodium octanoate and zinc/potassium octanoate, respectively, which agree with literature data (24.03 and 20.85 Å, respectively [11]). A unit cell dimension found for zinc/potassium octanoateis close to the value reported for zinc octanoate (20.83 or 20.88 Å) [9, 11].

The FTIR spectrum of zinc/sodium octanoate (Fig. 1b, *I*) displays bands at 1395 and 1410 cm⁻¹, due to symmetric carboxylate vibration; at 1597, 1607, and 1624 cm⁻¹, ascribed to asymmetric carboxylate vibration; and at 2872, 2857, 2850, 2923, 2957, and 2964 cm⁻¹, attributed to C–H stretching vibration of CH₂ and CH₃.

The FTIR spectrum of zinc/potassium octanoate (Fig. 1b, 2) presents bands at 1386 and 1397 cm⁻¹, corresponding to symmetric carboxylate vibration; at 1598 and 1624 cm⁻¹, assigned to asymmetric carboxylate vibration, and at 2854, 2871, 2925, and 2958 cm⁻¹, referring to C–H stretching vibration of CH₂ and CH₃ [11, 12]. Splitting of the carboxylate bands in the FTIR spectra of both octanoates results from two non-equivalent carboxylate moieties, in which the sodium or potassium and zinc atoms share the carboxylate groups [11, 12].

Considering that zinc/sodium and zinc/potassium octanoates are isostructural with zinc/sodium hexanoate, the Zn atoms in the layers of the materials have tetrahedral coordination and are bonded to four different carboxylates *via* an oxygen atom of each carboxylate ion (monodentate form). The other oxygen atoms of each carboxylate ion are bonded to sodium or potassium atoms that occupy octahedral sites, and therefore bonded to six different carboxylate ions.

The TGA curve of zinc/sodium octanoate reveals a mass loss of 3.9% up to 215°C, attributed to the loss of adsorbed water. In this same temperature range, the low-intensity DSC endothermic peaks emerging at 50 and 114°C are associated with the enantiotropic phase transitions and melting point. An endothermic peak at 202°C is also evident in the DSC curve (Fig. 2a). Equivalent peaks arise almost in the same positions for zinc/potassium octanoate and correspond to a mass loss of 3.7% (Fig. 2b).

For zinc/sodium octanoate, various exothermic peaks appear near 400°C, the same picture characterizes zinc/potassium octanoate (Fig. 2b). Heating zinc/sodium octanoate to 800°C produced a residue (dry basis) that accounts for 28.04% of initial sample weight. As for zinc/potassium octanoate, the experimental residue produced by heating to 500°C makes up 30.14% of initial sample weight. Both residual materials consist of a mixture of ZnO and alkali metal carbonates, which subsequently begin to decompose



Fig. 2. Thermal analysis (TGA/DSC) curves of zinc/sodium octanoate (a) and zinc/potassium octanoate (b).

at 900°C, a process that is not complete even at 1000°C. Based on the optimal formulas of the materials, $A_2[Zn(C_8H_{15}O_2)_4]$ (A = Na⁺ or K⁺), and considering the presence of ZnO and the respective carbonates in the final residues, the theoretical values for residues should correspond to 27.39 and 30.65% of the initial sample weight of zinc/potassium and zinc/sodium octanoates, respectively, so the deviations from the expected values are 2.3 and 1.7%, respectively.

High-resolution DSC measurements helped to study the phase transitions observed in the TGA curves more systematically (Fig. 3). Multiple phase transitions occur in both zinc/sodium octanoate (Fig. 3a) and zinc/potassium octanoate (Fig. 3b); these transitions resemble those observed for zinc carboxylates [13, 14]. The first heating effect indicates water loss from the sample, which cannot be observed during the second heating. Other structural phase transitions resemble transitions experienced by europium carboxylates [15].

In an enantiotropic polymorphic system, transition between two phases happens below the melting temperatures of the two phases. In the second and third heating/cooling cycles, these transitions probably cor-



Fig. 3. DSC curves of zinc/sodium octanoate (a) and zinc/potassium octanoate (b). *1*, *2*, and *3* are the first, second, and third heating/cooling cycles, respectively.

respond to transitions associated with layered crystalphases I and II (enantiotropic transitions) and isotropic liquid-phase 2 (melting) [13, 14]. During the first

Table 1. Ester conversions*

heating, zinc/sodium octanoate (Fig. 3a) undergoes four phase transitions at 73, 97, 102 (shoulder), and 118°C. Hysteresis leads to peaks at 44 and 79°C in the first and second cooling steps, and transitions at 58, 82, 95, and 115°C emerge in the second and third heating steps.

In the second heating/cooling cycle of zinc/potassium octanoate, two phenomena with an enthalpy of 11.58 J/g take place during heating, whereas the enthalpy of cooling is 15.35 J/g. Therefore, the processes can be considered as partially reversible.

For zinc/potassium octanoate (Fig. 3b), peaks appear at 50 and 115°C at the first heating step, while only one peak emerges at 78°C during cooling. At the second and third heating steps, peaks at 41 and 113°C arise, and only one peak appears at 79°C during the cooling step. Zinc/sodium octanoate and zinc/potassium octanoate melt at 118 and 115°C in the first heating step, respectively, and at 115 and 113°C in the other steps, respectively.

Table 1 lists the results of the esterification of octanoic acid with isopropanol catalyzed by the prepared octanoates.

Reactions were carried out at a temperature above the melting point of both octanoates to ensure that they acted as catalysts in the liquid phase; i.e., dispersed in solution, leaving the Zn^{2+} ions available to participate as catalyst. In literature an extensive information can be found analyzing the features of the reaction medium with octanoates [5, 6, 16, 17]. The alcohol/acid mixture, before esterification, has a totally homogenous nature. The alcohol/acid/ester/water mixture, obtained after esterification, also has a homogenous character. Therefore, it is deducted that water formed in the reaction cannot significantly affect the solubility of octanoic acid in isopropanol. Both materials afford high conversions: 52.2 and 54.2% for zinc/sodium octanoate and zinc/potassium octanoate, respectively, corresponding to conversion gains of 30.1 and 32.1%, respectively.

No.	Catalyst	Conversion	Conversion gain**
		%	
1	Zn/Na octanoate	52.2	30.1
2	Zn/Na octanoate (first reuse)	43.1	21.0
3	Zn/K octanoate	54.2	32.1
4	Zn/K octanoate (first reuse)	52.6	30.5
5	Zinc octanoate	50.7	28.6
6	Without catalyst	22.1	_

* All the experiments were performed under the following conditions: isopropanol/octanoic acid molar ratio = 8 : 1, catalyst/octanoic acid ratio = 7 wt %, temperature 155° C, and reaction time 2 h.

** Conversion gain was obtained by subtracting the catalytic conversion from the thermal conversion (experiment 5 was conducted without catalyst).

The esterification reaction is nearly thermoneutral, as calculated from the enthalpies of formation of different esters, acids and alcohols. The average value of ΔH° is -3 ± 2 kJ/mol. A heat flux of only 0.8 kW would be generated, if these processes were designed to take place with a mean conversion rate of 1 kmol/h. From the calculation of the effect of temperature on the degree of esterification with the Van't-Hoff's equation, 0.4% decrease is expected around ambient temperatures for the equilibrium constant per one Kelvin increase [18].

However, some results [19] show that, when the reaction conditions correspond to the equilibrium state, the water produced in the reaction is mainly distributed in an alcohol-rich phase, with a small amount remaining in an ester-rich phase. The presence of water in a monophasic system would shift reaction equilibrium to the reactants because of the hydrolysis reaction. However, when two liquid phases are considered, the water formed in the reaction medium is not available in the ester-rich phase, allowing the reaction to proceed to products. This fact therefore provides an explanation for the situation, when the experimental results exceed the calculated data.

Reuse tests (Table 1, first reuse) demonstrate that after the first reaction the catalytic activity of zinc/sodium octanoate and zinc/potassium octanoate decreases from 52.2 to 43.1% and from 54.2 to 52.6%, respectively. X-ray diffraction helped to investigate the catalysts recovered after the first reaction (Fig. 4).

After the first esterification reaction, zinc/sodium octanoate with a lattice constant of 23.94 Å (Fig. 4a, 1) is transformed into a material with a unit cell parameter of 20.89 Å close to the interplanar spacing of zinc octanoate (Fig. 4a, 2), the XRD peaks shift slightly to higher angles as compared to peak positions of zinc octanoate characterized by the unit cell constant of 21.14 Å (Fig. 4a, 3). Zinc/potassium octanoate having a lattice dimension of 20.77 Å (Fig. 4b, 1) partly preserves its structure with a lattice parameter of 20.91 Å (Fig. 4b, 2) with a fraction of this material transformed into zinc octanoate identified by an interplanar spacing of 21.19 Å (Fig. 4b, 2). Our measurements indicated 21.14 Å as the interplanar spacing of zinc octanoate (Fig. 4b, 3) whereas the literature reports lattice dimensions of 20.88 Å [11] and 20.83Å [9]. It appears that the lattice dimensions are subject to variations, the range of which depends on the conditions used to synthesize the sample and on sample positioning in the sample holder during data collection.

To test the hypothesis that zinc/sodium octanoate and zinc/potassium octanoate are transformed into zinc octanoate during the esterification reactions, zinc octanoate was used as catalyst under the same experimental conditions (Table 1, entry 5). A catalytic conversion of 50.7% and a conversion gain of 28.6% were obtained, which are close to the values obtained for zinc/sodium octanoate in the first reuse (catalyzed



Fig. 4. X-ray diffraction patterns of zinc/sodium octanoate (a) and zinc/potassium octanoate (b) before (2) and after use as catalyst in the esterification of octanoic acid with isopropanol (1). (3) Zinc octanoate.

conversion of 43.1% and conversion gain of 21.0%). This difference in catalytic conversions is presumably due to a smaller number of zinc sites in the "zinc/sodium octanoate" taken from the first reuse. As for zinc/potassium octanoate in the first reuse, conversion and conversion gain were 52.6 and 30.5%, respectively. These results can be explained by partial conversion of the starting zinc/potassium octanoate to zinc octanoate. Given that zinc/potassium octanoate and zinc octanoate are characterized by the different level of catalytic activity, an intermediate value of activity can be expected from the mixture.

The FTIR spectra of zinc/sodium octanoate (Fig. 5a, I) and zinc/potassium octanoate (Fig. 5b, I) are different, but the spectra recorded for the catalysts recovered after the first esterification reaction are similar (Figs. 5a, 2 and 5b, 2) and retain the similarity after the first reuse (Figs. 5a, 3 and 5b, 3). Hence,







Fig. 5. FTIR spectra of zinc/sodium octanoate (a) and zinc/potassium octanoate (b) before (1) and after use as catalyst the first esterification reaction between octanoic acid and isopropanol (2) and after the first reuse (3). 4—Zinc octanoate.

during esterification, zinc/sodium octanoate and zinc/potassium octanoate are transformed into the same compound, the FTIR spectrum of which contains the same bands as the FTIR spectrum of zinc octanoate (4).

To confirm that the material isolated after the esterification reactions is actually zinc octanoate, the material derived from zinc/potassium octanoate was submitted to TGA/DSC analysis. The results of the analysis not shown in this work can nevertheless be compared with TGA/DSC data available for zinc octanoate.

In contrast to the TGA/DSC analysis of zinc/potassium octanoate before its use as catalyst in the esterification reaction (Fig. 4b), the material isolated after the reaction is anhydrous and does not experience significant mass loss up to about 180°C. Two endothermic



Fig. 6. EDS spectra of zinc/sodium octanoate (1), zinc/potassium octanoate (2), and recovered after the esterification of octanoic acid with isopropanol the zinc/sodium octanoate (3) and zinc/potassium octanoate (4).

peaks at 116 and 136°C correspond to phase transitions in the solid state. Two large exothermic peaks at 290 and 343°C correspond to decomposition of the material and ZnO formation. Similarly, the TGA/DSC curve of pure zinc octanoate not shown in this work displays three small endothermic peaks at 101, 120, and 136°C in addition to an exothermic peak at 383°C.

The weight of the final residues formed after octanoates were used as catalysts in the esterification reaction was expected to be 20.06% for zinc octanoate and 20.96% for zinc/potassium octanoate. These values are lower than the experimentally found amount of 23.13%. Adsolubilization of some organic material between the pillars of intercalated octanoate anions (in this case, potassium octanoate) possibly occurs. Indeed, adsolubilization of neutral organic molecules between pillars of surfactants in layered double hydroxides (LDH) has already been described [20, 21]. Therefore, this technique also suggests that zinc/potassium octanoate is transformed into zinc octanoate in situ during the esterification reaction.

To corroborate the facts verified by FTIR and TGA/DSC, EDS analysis of the catalysts before and after the esterification reactions was conducted (Fig. 6). According to the EDS spectra the starting catalysts contain sodium or potassium, carbon, oxygen, and zinc, whereas the catalysts recovered at the end of the esterification reactions contain only carbon, oxygen, and zinc. Along with FTIR and TGA/DSC results, the EDS data confirm that zinc/sodium octanoate and zinc/potassium octanoate are converted into zinc octanoate during the esterification reaction.

As for the characterization of the starting solids by SEM, with results not shown in this work, the structure of these materials expectedly encompasses stacked layers. The crystals of both zinc/sodium octanoate and zinc/potassium octanoate resemble plates. The particles located over the planes of the layered crystals are much larger than the particles accommodated along the stacked layers.

Finally, in order to prove that zinc/sodium octanoate and zinc/potassium octanoate were really transformed into zinc octanoate after they were used as catalysts in esterification reactions, the materials recovered at the end of esterification were analyzed using the DSC technique.

Based on the results derived from the DSC measurements and not shown in this work, on the first heating zinc/sodium octanoate and zinc/potassium octanoate isolated after use as catalyst display two endothermic peaks at 121 and 139°C, and two exothermic peaks at 93 and 113°C. In the second and third heating runs, three endothermic peaks occur at 100, 139, and 199°C, and two exothermic peaks are exhibited at 93 and 113°C in the course of the second cooling.

DSC curves obtained for zinc octanoate and not shown in this work indicate that during the first heating run two endothermic peaks appear at 95 and 127°C, and two exothermic peaks occur at 65 and 47°C in the course of the first cooling. Following the second and third heating runs, three endothermic peaks at 62, 90, and 122°C occur, and the same peaks were observed on the curve obtained after the first cooling appear on the second cooling. The literature brings more details of the attribution of phase transitions undergone by zinc octanoate [13, 14].

Since the thermal behavior of starting zinc/sodium octanoate and zinc/potassium octanoate is markedly different from that shown by pure zinc octanoate (Fig. 4a,b), it was concluded that both starting materials are unstable and are transformed into zinc octanoate during the esterification reactions. However, the reasons of different thermal behavior of the catalysts recovered after transesterification and that of zinc octanoate remain unclear. It can be speculated that the recovered catalysts are alternative forms of zinc octanoate, in which stronger intermolecular forces between carbon chains are developed. Accordingly, additional energy efforts are needed to approach phase transitions on heating with solid structures recovered at higher temperatures.

Finally, the reaction mechanism proposed for the synthesis of isopropyl octanoate with zinc octanoate is similar to that described in literature for esterification of fatty acids using heterogeneous zinc catalysts. However, the hydrophobic homogeneous mode of action of lamellar carboxylates can be taken into account. It can be postulated that at the initial step the acid-base interaction between the zinc atom from the catalyst and the carbonyl group from the octanoic acid generates a positive charge of high density on the carbonyl group in order to form a tetrahedral intermediate. Then, a proton is transferred between the oxygen

atoms of this intermediate, producing a water molecule. This molecule is eliminated as a result of formation of isopropyl octanoate. Finally, as the acid-base interaction between the zinc atom from the catalyst and the carbonyl group from isopropyl octanoate falls off this zinc atom is free to begin another catalytic cycle [5-7, 22].

However, in the case of zinc/sodium octanoate and zinc/potassium octanoate, the sodium and/or potassium atoms are also available for the acid-base interaction between sodium and/or potassium atom from the catalyst and the carbonyl group from the octanoic acid. Therefore, unlike pure zinc octanoate, zinc/sodium octanoate and zinc/potassium octanoate have two kinds of catalytically active sites, the zinc atom and the sodium and/or potassium atom. This accounts for the difference in the catalytic activities of zinc/sodium octanoate, zinc/potassium octanoate and zinc octanoate.

CONCLUSIONS

Both Na₂[Zn(C₈H₁₅O₂)₄] and K₂[Zn(C₈H₁₅O₂)₄] were synthesized, characterized, and showed promising catalytic activity in the esterification of octanoic acid with isopropanol under the following conditions: isopropanol/octanoic acid molar ratio = 8 : 1, catalyst/octanoic acid ratio = 7 wt %, temperature 155°C, and reaction time 2 h. Both catalysts are converted to zinc octanoate during esterification. It was concluded that the materials tested as catalysts possess characteristics of both heterogeneous and homogeneous catalysts, although they are converted into zinc octanoate during the reaction.

ACKNOWLEDGMENTS

The present work received financial support from CNPq, Conselho Nacional de Desenvolvimento Científico e Tecnológico (Brazil) through postdoctoral grant process number 168161/2014-1. The financial funding by CAPES and FINEP is also acknowledged.

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