Kinetics and Catalysis, Vol. 43, No. 4, 2002, pp. 536–541. Translated from Kinetika i Kataliz, Vol. 43, No. 4, 2002, pp. 580–585.
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Application of Mechanochemical Catalysis to the Synthesis of Boric Acid Esters

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Received August 6, 2001

Abstract—The syntheses of triisopropyl borate and other boric acid esters under conditions of mechanochemical activation with the use of zeolite catalysts were found to be highly efficient. The proposed method exhibits the following advantages over known methods: short synthesis times, low energy consumption, higher yields of target products, and the absence of byproducts. The mechanism of the catalytic esterification of boric acid under conditions of mechanochemical activation is discussed.

INTRODUCTION

Previously [1], the term mechanochemical catalysis was introduced, which implies catalytic reactions performed under conditions of mechanochemical activation. Mechanochemical catalysis differs from other types of catalysis in that energy for performing reactions is supplied as mechanical energy. This branch of science is very poorly understood; to the best of our knowledge, only ten publications, which were cited in the review [1], have been devoted to this subject matter. The aim of this work was to extend the range of the applicability of mechanochemical catalysis and to find new efficient methods for the synthesis of boric acid esters.

The high reactivity of boric acid esters is responsible for their use as reagents for new methods of organic synthesis and for the protection of functional groups in organic synthesis. They are widely used as catalysts for many chemical reactions such as the selective oxidation of aliphatic hydrocarbons to alcohols and of aromatic hydrocarbons to phenols, the epoxidation and polymerization of olefins, and the isomerization of unsaturated alcohols. They are used as additives for improving the heat resistance of textile fibers, woven fabrics, etc. The boric acid esters of polyoxo compounds are efficient fungicides and antiseptics [2–4].

The well-known methods for the preparation of boric acid esters were developed based on the chemical reactions of orthoboric acid, borax, boron oxide, or boron trichloride with alcohols. The main preparation methods for boric acid esters were described previously [5, 6]:

$$3ROH + BCl_3 = (RO)_3B + 3HCl,$$

$$6ROH + (CH_3COO)_4B_2O = 2(RO)_3B + 4CH_3COOH + H_2O,$$

$$3ROH + H_3BO_3 = (RO)_3B + 3H_2O,$$

$$6ROH + B_2O_3 = 2(RO)_3B + 3H_2O,$$

$$3ROH + NaBH_4 + H^+ = (RO)_3B + 4H_2 + Na^+,$$

$$3ROH + (R^1O)_3B = (RO)_3B + 3R^1OH,$$

$$3ROH + B_2O_3 = (RO)_3B + H_3BO_3.$$

However, the simplest method for preparing alkyl borates is the interaction of boric acid or boron oxide with alcohols with the azeotropic distillation of water [2, 7]:

$$3ROH + H_3BO_3 = (RO)_3B + 3H_2O,$$

$$3ROH + 1/2B_2O_3 = (RO)_3B + 3/2H_2O.$$

In this case, the yields of esters depend on the chemical nature of alcohols (Table 1). It can be seen in Table 1 that isopropyl borate is most difficult to prepare. The main goal of this study was to develop a method for preparing isopropyl borate.

We believed that the reaction of boron oxide with 2-propanol is the most appropriate method for the synthesis of isopropyl borate because the least expensive and least toxic reagents are used in this case and the lowest amount of water, which leads to the hydrolysis of esters, is formed. Difficulties expected in performing this reaction consist in the removal of formed water and in the necessity of accelerating mass-transfer processes (because a heterogeneous reaction between a liquid and a solid takes place) and increasing the reactivity of boron oxide (because is it sparingly soluble in alcohols, and the reaction occurs at the interface rather than in solution). We believed that all of these problems could be solved by performing the reaction under conditions of MCA with the use of spherical zeolite granules as grinding bodies, catalysts, and water absorbents. The formation of trace diisopropyl ether $(CH_3)_2CHOCH(CH_3)_2$, as well as mono- and diisopropyl borates, which are undesirable impurities in the use of triisopropyl borate for particular purposes, in the

presence of acid catalysts at elevated temperatures presents another problem that should be taken into consideration. It is well known from published data [8–10] that the use of protic acids as catalysts did not accelerate the reactions; however, in this case, alcohols were involved into various side reactions with the formation of water. According to the reaction thermodynamics, this resulted in an effect that is in direct opposition to the expectations. Because of this, we used zeolites in cationic form to minimize the expected adverse effect of proton sites.

EXPERIMENTAL

Mechanochemical activation was performed in an AGO-2 planetary centrifuge mill at a rotation frequency of 10–17 s^{-1} for 1–30 min. The drums of the mill were charged with 50 g of the spherical granules of zeolite NaA, zeolite NaX, or the Zeokar 2 catalyst containing zeolite Y. The zeolites were precalcined at 300°C for 5 h to remove water. The drums were charged with 7 g of boron oxide of high-purity grade and 36 g of an alcohol (ethanol, 2-propanol, or 2-butanol) of reagent grade in addition to zeolites. The alcohols were predried with zeolite NaX.

The reaction products were analyzed by ^{1}H NMR spectroscopy with the use of Bruker MSL-400 and DPX-250 spectrometers. The degrees of conversion of starting alcohols were calculated from the intensity ratios between signals due to the protons of alcohols and esters. The conversion (X) was calculated by the equation $X = A/(N + A)$, where A is the peak intensity of a proton at the carbon atom bound to the ester group in $((CH_3)_2C\mathbf{H}O)_3B$ and N is the peak intensity of a proton at the carbon atom bound to the hydroxyl group in $(CH_3)_2C\mathbf{H}OH$ (the corresponding atoms are boldface).

After performing the reaction, the zeolites and boron oxide were studied by X-ray diffraction analysis for determining the retention of the crystal structure of zeolites and possible defect formation in boron oxide. The X-ray diffraction patterns were obtained on an HZG-4C diffractometer with the use of CuK_α radiation and a graphite monochromator.

The concentrations of aprotic sites in zeolites were determined by EPR spectroscopy according to the procedure described previously [11]. The tetramethyl-1-piperidinyloxy (TEMPO) nitroxyl radical was used as a paramagnetic probe.

RESULTS AND DISCUSSION

The test reactions were reversible under the conditions of our experiments, and the chemical nature of an alcohol had an insignificant effect on the equilibrium degree of conversion. This statement is based on the results of thermodynamic calculations performed with the use of published data [9, 12] (Table 2). Table 2 indicates that the conversion was no higher than 30%. It is clear that the introduction of zeolites into the reaction zone will increase the degree of conversion because of water removal from the reaction medium.

Table 1. Preparation conditions and yields of boric acid esters [5–7]

Boric acid ester	Reaction temperature, °C	Time, h	Yield, %
Propyl	83	8	95
Isopropyl	73	18	30
Butyl	113–122	4	95.6
Isobutyl	114	5	93
Isoamyl	124–150	3	95

Table 2. Calculated equilibrium conversions and equilibrium constants (K_p^{298}) for the synthesis of trialkyl borates

Alcohol	K_p^{298}	Equilibrium conversion, %
Methanol	800	26.0
Ethanol	1000	27.0
2-Propanol	1700	28.5
Butanol	2300	29.6
2-Butanol	1800	28.8

First, two experiments were performed to be certain that the mechanochemical method is advantageous. In one experiment, a mixture with the component ratio specified in Experimental was boiled for 3 h; in this case, the conversion of 2-propanol was 10–12%. In the other experiment, the MCA of a mixture of the alcohol and boron oxide was performed using metal balls in the absence of zeolite; the formation of the boric acid ester was not detected after activation for 30 min.

With the use of spherical zeolite granules as grinding bodies, considerable conversions were observed even at short activation times (Table 3). Table 3 summarizes the conversion of 2-propanol depending on the time and intensity (drum rotation frequency) of MCA with the use of zeolite NaX as a catalyst. Table 3 indicates that the conversion only slightly depends on the rotation frequency of drums, and it is 30% or higher even at short activation times. Recall that such degrees of conversion are attained in several hours with the use of traditional synthetic methods (Table 3 and the above data on boiling in the presence of zeolite).

The kinetic curves plotted using data from Table 3 exhibit the following three regions (Fig. 1): an initial portion with a high rate of alkyl borate formation (MCA time of 1 to 2 min), a region of a smooth increase in the degree of conversion (MCA time of 2–15 min), and a region of flattening out (MCA time of 15–30 min).

The high rates of alkyl borate formation at the initial stage of activation can be due to the activation of an amorphous portion of boron oxide. The point is that

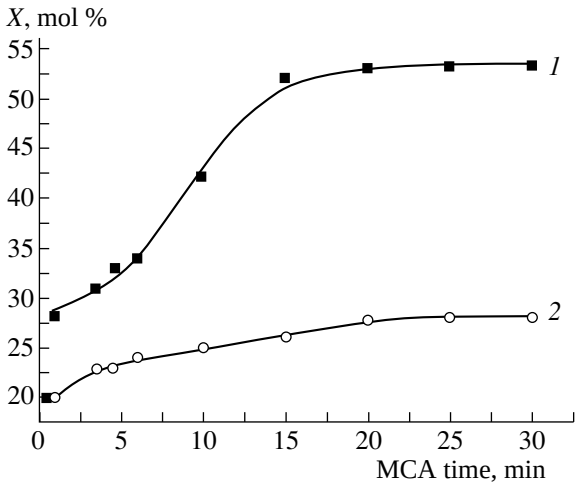

Fig. 1. Conversion of 2-propanol (*X*) on zeolites (*1*) NaX and (*2*) NaA under conditions of MCA.

boron oxide used as the reagent consists of two phases: crystalline and X-ray amorphous (Fig. 2). We attempted to detect changes in these phases in the course of activation. To prevent the relaxation of structural changes in the course of chemical reactions, the activation of boron oxide with zeolite granules was performed in a pentane medium, a liquid that is similar to 2-propanol in viscosity, however, inert toward boron oxide. We failed to detect any changes in the crystalline phase due to MCA under the specified conditions by X-ray diffraction analysis. However, the amorphous phase underwent changes: it was crystallized upon activation in pentane for 1 min. This is a very unusual fact for the processes of mechanical activation because the inverse processes of amorphization of crystalline substances under the action of MCA were described in the literature. Thus, the amorphous phase underwent a structural rearrangement in the course of which the reactivity of boron oxide can increase. According to published data [13], the amorphous phase has a layered structure. By analogy with known data on the activation of layered compounds [14, 15], it is believed that, at short activation times, shear defects are formed in this structure, and they are responsible for the increase in the reactivity. Presently, it is impossible to provide an experimental support to this hypothesis because of the absence of appropriate procedures for studying amorphous substances.

Table 3. Conversion of 2-propanol depending on the time of MCA and the rotation frequency of drums

MCA time, min	Conversion, %		
	10*, s^{-1}	14*, s^{-1}	17*, s^{-1}
1	27	28	28
3.5	3	31	3
4.5	3	33	3
6	32	34	4
10	43	42	42
15	46	52	44
20	52	53	47
25	52	53	47
30	53	53	5

* Drum rotation frequency.

At the second stage of MCA, the rate of formation of the boric acid ester decreased. This can be associated with either the disappearance of shear defects because of the breakage of the amorphous phase along these defects, as it was observed in zinc oxide and graphite [14, 15], or a decrease in the reactivity of boron oxide due to crystallization because, as a rule, amorphous compounds are more highly reactive. Another conceivable reason for the decrease in the activity might be zeolite destruction in the course of MCA, as we observed in the MCA of zeolite FeZSM-5. However, the X-ray diffraction analysis of a zeolite sample after performing the reaction demonstrated that the zeolite structure did not undergo degradation under the given activation conditions (Table 4). The inconsistency between peak intensities is due to a considerable decrease in the intensity of a diffraction maximum with d = 1.4455 nm because of alcohol sorption in zeolite channels.

The kinetic curve at this portion is adequately described by a first-order rate equation (Fig. 3). This appears explicable because one of the reactants occurs in a solid state. The curve demonstrates that boron compounds present in solution have almost no effect on the course of the reaction; otherwise, the reaction rate should be described by a second-order or more complex equation. These data will be used below for describing the suggested reaction mechanism of esterification under conditions of MCA.

The appearance of a plateau in the kinetic curve should also be explained. The moisture capacities of zeolite samples were determined to be 0.42 and 0.34 g/g for NaX and NaA, respectively. Based on these values, the simplest calculations demonstrated that at 100% conversion the released water can be completely absorbed by zeolite and the reaction equilibrium should be shifted toward the formation of esters. However, we observed a steady state in the system at conversions far from 100%. It is likely that water and alcohols compete in the course of their sorption by zeolites; an equilibrium in this competition is responsible for the highest possible conversions that can be attained under our conditions.

The yields of boric acid esters essentially depend on the nature of catalyst in use or, more precisely, on the nature of zeolite that forms the basis of the catalyst. This is illustrated by data given in Table 5.

Nonzeolite catalysts such as alumina and silica gel exhibited no activity under our reaction conditions.

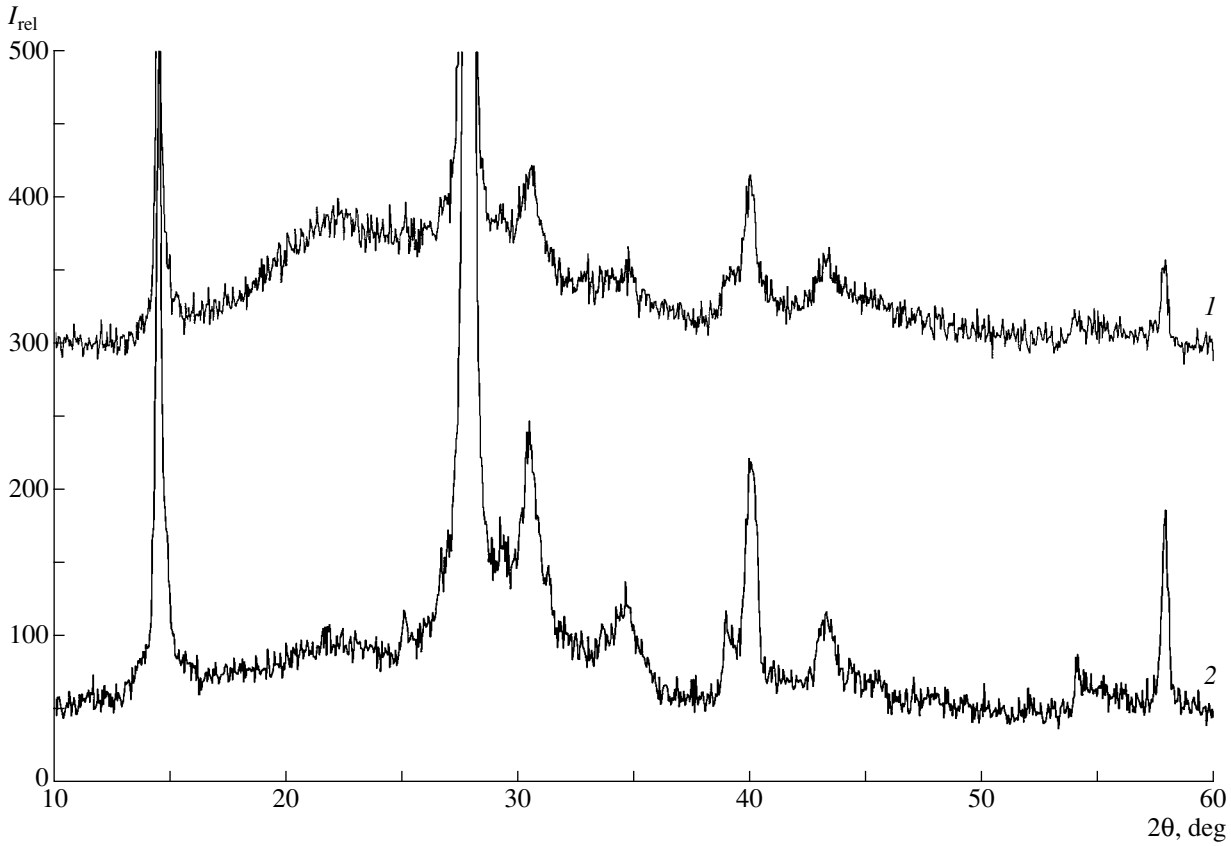

Fig. 2. X-ray diffraction patterns of (*1*) initial boron oxide and (*2*) boron oxide mechanically activated for 1 min.

It is clear that differences in the catalytic activity are associated with the acid properties of zeolites. As mentioned above, proton sites insignificantly affect the main reaction and accelerate side reactions. To check this under our conditions, we performed cation exchange to convert the sodium form of zeolite A into the H form. The determination of the catalytic activity of zeolite HA demonstrated that the exchange left it almost unaffected (Table 5), and the formation of byproducts was not detected. This fact allowed us to conclude that the catalytic action of zeolites depends on the presence of aprotic acid sites. In this case, the above sites occur on the outer surface of zeolite granules because only this surface is in contact with the reactants in the course of MCA.

The above hypothesis was supported in part by the determination of the concentration of Lewis acid sites. This concentration can be reliably determined by the titration of zeolites with solutions of free radicals until the detection of the free radicals in solution. This procedure was described in detail as applied to a study of aprotic acid sites in alumina [11]. We used TEMPO solutions in pentane to determine the concentration of the sites. Note that the molecular size of TEMPO does not allow the molecule to enter zeolite channels, and the measured concentration refers to the outer surface of zeolite. The data obtained exhibited a qualitative correlation between the concentration of Lewis acid sites and the catalytic activity of zeolites NaA and NaX (Table 6). The fact that this correlation is due to sites on the outer surface will be used below for describing a hypothetical reaction mechanism of boron oxide esterification under conditions of MCA.

Table 4. X-ray diffraction patterns of zeolite NaX before and after the reaction (MCA time, 30 min; drum rotation frequency, 14 s^{-1})

hkl	Before MCA		After MCA	
	d, nm	*I*, %	*d*, nm	*I*, %
111	1.4455	100	1.4441	52
220	0.8845	17	0.8840	26
311	0.7538	13	0.7527	20
331	0.5738	25	0.5724	51
333	0.4806	10	0.4795	30
440	0.4415	20	0.4419	37
531	0.4237	1	0.4226	2
620	0.3943	5	0.3937	9
533	0.3805	60	0.3808	100

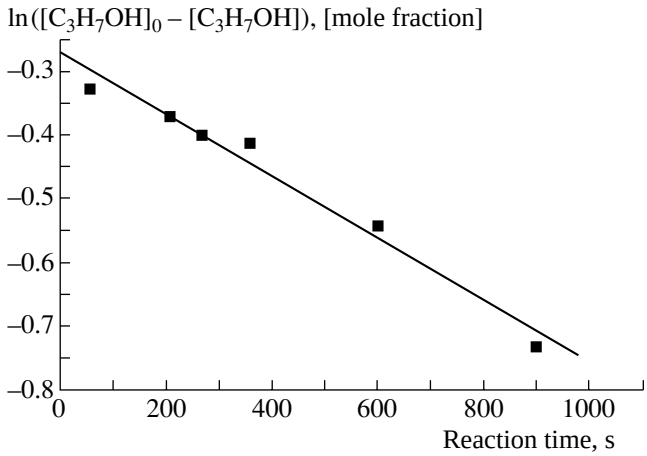

Fig. 3. Logarithm of the concentration of isopropanol as a function of esterification reaction time.

The deviation observed in the catalyst Zeokar 2 (Table 6) is due to the fact that it has a complex phase composition. In addition to zeolite Y, it contains other compounds that bear Lewis acid sites; however, these compounds are inactive under the given reaction conditions. The assumption that not every aprotic acid site is active was supported by the inactivity of A-1 alumina. For some reasons, aprotic acid sites in the zeolite structure are active in the esterification reaction under conditions of MCA. Thus, if the zeolite fraction in the catalyst Zeokar 2 is taken into account, a qualitative correlation also takes place in this catalyst.

Table 5. Activities of zeolites NaA and NaX and the Zeokar 2 zeolite catalyst in the reaction of isopropyl borate formation (rotation frequency of 17 s^{-1})

MCA time, min	Conversion of 2-propanol, mol %			
	NaA	HA	NaX	Zeokar 2
0.5	16	–	20	12
1	20	19	28	14
3	23	22	30	16
5	23	23	30	18
7	24	23	40	20
10	25	24	42	22
15	26	26	44	23
20	28	27	47	23
25	29	28	48	24
30	31	–	50	24

Table 6. Catalytic activity depending on the concentration of aprotic acid sites

Catalyst	Concentration of sites, g^{-1}	Conversion, mol %
NaA	4.0×10^{17}	29
NaX	9.1×10^{17}	50
Zeokar 2	9.7×10^{17}	24

In addition to triisopropyl borate, other esters can also be prepared with the use of this method, as illustrated by Table 7. It is most likely that lower conversions of 2-butanol are associated with its high viscosity, as a result of which the intensity of MCA is considerably decreased.

As for the reaction mechanism, it can be considered only hypothetically because measurements in the course of MCA are technically impossible to perform. The main results that form the basis for our notions of the reaction mechanism are the following:

The reaction does not occur under conditions of MCA in the absence of catalysts.

Zeolites are effective as catalysts, whereas Al_2O_3 and SiO_2 are inactive.

The reaction occurs more efficiently under conditions of MCA.

The replacement of alkali metal cations in zeolites by protons has no effect on the catalytic activity.

Boron compounds present in solution have almost no effect on the course of the reaction, and solid boron oxide mainly participates in the reaction.

A correlation between the catalytic activity and the concentration of aprotic acid sites on the outer surface of zeolites is observed.

Based on the above data, it is believed that the chemisorption and activation of alcohols takes place at the aprotic acid sites of the outer surface of zeolite granules. It is likely that not only aprotic acid sites that were initially present in zeolites but also sites that can be formed in the course of MCA take part in the reaction. A fresh surface of boron oxide and reactive sites as crystal structure defects at the surface of crystallites are formed in the course of MCA. The formation of boric acid esters takes place at the instant the surface of a zeolite granule makes contact with the layer of a chemisorbed alcohol and the reactive sites of boron oxide. We are aware that this mechanism was not reliably supported by experimental data; however, it is most consistent with the observed behavior.

Thus, we found a new highly efficient method for preparing trialkyl borates. It is favorably characterized by short reaction times and low energy consumption. As compared with known methods, the synthesis time is shortened from several tens of hours to a few minutes at comparable energy inputs per unit time. The yield of esters increases from 25–30% for known methods to 50%. Byproducts are not formed. We found that the yield of target products essentially depends on the

Table 7. Catalytic activity of zeolite NaA in the reaction of boric acid ester formation under conditions of MCA (drum rotation frequency of 17 s^{-1})

MCA time, min	Alcohol conversion, mol %		
	ethanol	2-propanol	2-butanol
1	15	20	11
3	20	23	12
5	24	23	14
7	28	24	16

nature of catalyst. It is reasonable to believe that aprotic acid sites in the zeolite structure are catalytically active sites. A hypothetical mechanism of catalytic reactions under conditions of MCA is proposed.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research, project no. 00-15-97440.

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