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Nano-K$_2$CO$_3$: Preparation, Characterization and Evaluation of Reactive Activities

Jun-Zhang Li, Shi-Ming Fan, Xuan-Fei Sun and Shouxin Liu*

Abstract: A novel base, nano-K$_2$CO$_3$, was easily prepared by ultrafine wet milling. The surface properties and the reactive activities of nano-K$_2$CO$_3$ were characterized. It was found that such base showed higher basicity than normal K$_2$CO$_3$ and could replace sodium (or potassium) alkoxide to carry out monoalkylation and oximation of active methylene compounds. The nano-K$_2$CO$_3$ could be regenarated and reused 10 times without loss of its reactive activity.

Introduction

The traditional strong base such as sodium (or potassium) alkoxide were used widely in organic synthesis industry, but these base have a number of shortcomings such as non-recovery, high cost, severe corrosion and more side reactions. K$_2$CO$_3$ is a good base because it is lowcost, noncorrosive and easy to separate from products in non-aqueous media. However, its low activity limits its efficiency in practical application. Recently, nano-materials as catalysts are receiving considerable attention because of their high specific surface area and special reactivities.[1] Compared with traditional heterogeneous reaction, nanocatalyst-based heterogeneous reaction can efficiently improve activity and selectivity, as well as enable transformations of reaction substrate under much more gentle conditions and products isolation.[2] Numerous nano-metals such as Pt, Pd, Mg, Cu, Ni, and their metal oxide have been widely applied in various organic reactions.[3] Many nano-inorganic salts such as alkaline-earth metals carbonate (MCO$_3$) have been reported,[4] but so far there is just a little of reports on nano-alkali metal carbonates (M$_2$CO$_3$).[5] We previously reported that the preparation of macronano-K$_2$CO$_3$ with average particle size of 266 nm.[6] In this work, we developed a simple method of preparing nano-K$_2$CO$_3$ with average particle size of 64 nm and used it as a base to evaluate its properties through the monoalkylation and oximation of active methylene compounds.

Results and discussion

Based on the ionic characteristics of K$_2$CO$_3$, nano-K$_2$CO$_3$ was prepared by ultrafine wet milling.[7] The particle size of nano-K$_2$CO$_3$ strongly depends on solvent, with polar and protic being more

Table 1 Effect of solvent on the preparation of nano-K$_2$CO$_3$

Entry	Solvent^a	Time^b (h)	Average size^c (nm)
1	Toluene	8	893
2	Acetonitrile	10	775
3	1-Butanol	10	581
4	Ethanol	8	266
5	Ethanol/0.1% Lauric acid^d	8	112
6	Ethanol/0.2% Lauric acid	8	64
7	Ethanol/0.3% Lauric acid	8	64

^{a} Solvent/potassium carbonate (molar ratio = 1.5:1). ^{b} Average size does not decrease with prolonged grinding time. ^{c} Average size was measured using a laser particle size analyzer. ^{d} Molar percentage of nano-K$_2$CO$_3$.

suitable for the preparation of nano-K$_2$CO$_3$ (Table 1, entries 3 and 4) than nonpolar and aprotic (Table 1, entries 1 and 2). A possible reason may be that polar solvents have strong electrostatic interactions with the charge of nano-K$_2$CO$_3$ surface to retard the agglomeration and contribute to the dispersion of nanoparticles. The anion of nano-K$_2$CO$_3$ surface can be intensively solvated by protic solvent through the interaction of hydrogen bond to decrease the surface energy of nanoparticle. Given the properties of hydroxyl bond in the dispersion and stabilization of nano-K$_2$CO$_3$ particles, lauric acid was selected as an auxiliary to prepare nano-K$_2$CO$_3$ with smaller particle size. When 0.1 % mol lauric acid was added to ethanol, K$_2$CO$_3$ particles obtained by milling obviously decreased (Table 1, entries 4 and 5). By controlling lauric acid with 0.2 % mol of ethanol, 64 nm nano-K$_2$CO$_3$ with average particle size (Table 1, entry 6) and narrow particle size distribution was prepared (ESI†; Fig S1). The SEM image of nano-K$_2$CO$_3$ is shown in Fig.1. Nano-K$_2$CO$_3$ was easily agglomerated when exposed to air. Hence, it was stored in the solvents of ethanol/0.2% Lauric acid and directly used for the reaction.

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†Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x
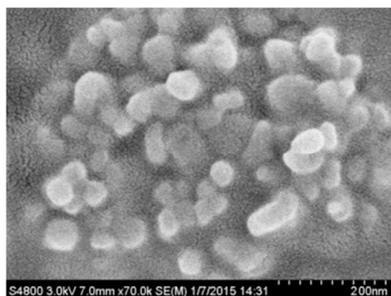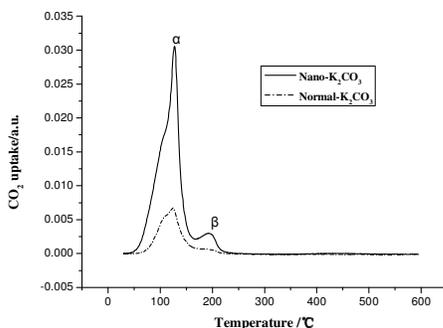
Fig. 1 SEM of nano-K_2CO_3 (64 nm)

Fig. 2 CO_2-TPD profiles of nano-K_2CO_3 and normal K_2CO_3

Table 2 Basic intensity of nano-K_2CO_3 and normal K_2CO_3

	CO_2 uptake (mmol/g)		
	α	β	Total basicity
Nano-K_2CO_3[a]	0.385	0.032	0.417
Normal K_2CO_3	0.105		0.105

[a] Sample was measured immediately after filtration and vacuum drying for 4 h at 120 °C

The basic strength and relative amount of surface basic sites on nano-K_2CO_3 were studied by CO_2-TPD (Fig. 2). CO_2-TPD peak area showed that the total capacity of CO_2 adsorption of nano-K_2CO_3 was four times higher than that of normal K_2CO_3 (Table 2). Obviously, the adsorption of nano-K_2CO_3 could be ascribed to its high specific surface area and characteristic surface property. For normal K_2CO_3, the desorption peak α located at around 60–160 °C interval was observed, which may be due to physisorption. However, two desorption peaks were observed for nano-K_2CO_3. Except for peak α, the other peak β located at around 170–220 °C was distinct, which could be due to the characteristic basic site caused by the exposed anion of nano-K_2CO_3 surface. This finding suggested that a new type of adsorption site with stronger basicity existed on nano-K_2CO_3 surface. Given the greater number of characteristic basic sites exposed on the surface, nano-K_2CO_3 activity was greatly improved.

To examine the chemical property of nano-K_2CO_3, monoalkylation and oximation of active methylene compounds were performed. The monoalkylation of active methylene compounds with alkyl halides is a very useful reaction for prolonging the carbon chain.[8] The Oximation of active methylene compounds with nitrous esters is a very important reaction for the preparation of oximes, which are particularly useful precursors for the synthesis of α-amino acids[9] and heterocyclic compounds[10]. Traditionally, both of these reactions often require a strong basic

Table 3 Monoalkylation of active methylene compounds

Entry	W_1	W_2	R-X	T (°C)	Time (h)	Yield (%)[a]
1	CO_2Et	CO_2Et	n-PrBr	65	8	85.2
2	CO_2Et	CO_2Et	EtBr	65	8	87.4
3	CO_2Et	CO_2Et	n-BuBr	65	8	82.6
4	CO_2Et	CO_2Et	$PhCH_2Cl$	65	8	89.3
5	CO_2Et	CO_2Et	$Br(CH_2)_3Cl$	65	8	87.5
6	CO_2Et	CO_2Et	$Br(CH_2)_5Cl$	65	8	85.8
7	Ph	CN	$BrCH_2CO_2Et$	75	15	62.4
8	Ph	CN	EtBr	75	15	69.5
9	CN	CN	EtBr	50	8	95.4
10	CN	CN	n-PrBr	50	8	95.3
11	CN	CN	n-BuBr	50	8	95.6
12	CN	CO_2Et	PhCH2Br	60	8	94.4
13	CN	CO_2Et	n-PrBr	60	8	90.6
14	CN	CO_2Et	n-BuBr	60	8	89.5
15	MeCO	CO_2Et	n-HexBr	70	10	80.8
16	MeCO	CO_2Et	n-BuBr	70	10	83.2
17	MeCO	CO_2Et	EtBr	70	10	85.3

[a] Yield of isolated product

medium, such as a solution of sodium alkoxide/alcohol. However, sodium ethoxide and sodium hydride is more expensive and lacks the selectivity for the alkylation of active methylene compounds, easily producing a mixture of mono- and di-alkylation products. In particular, a amount large of wastewater was produced during work-up in chemical industry. In this work, nano-K_2CO_3 was used as a base in nonaqueous media to replace to sodium alkoxide or sodium hydride and carry out both reactions. Both heterogenous reaction systems of monoalkylation and oximation of active methylene compounds were successfully constructed.

The alkylation of diethyl malonate with n-propyl bromide was initially examined. When 1.3 equiv. of nano-K_2CO_3 was used as base, the product was achieved in 85.2% yield at 65 °C (Table 3, entry 1). However, the reaction occurred in the presence of a large excess of normal potassium carbonate (3.5 equiv.), the product was obtained in 65% yield after 8 h at 75 °C.

To further explore the scope and limitations of this method, various active methylene compounds (W_1, W_2 = CO_2Et, CN, MCO, Ph) and alkyl halide were also examined (Table 3). Surprisingly, in all cases, the products of *O*-alkylation and dialkylation that occurred when using usual base were not detected.[11]

The reaction system exhibited higher chemical and regioselectivity in good and excellent yields. Thus, the less active compound phenylacetonitrile, as the active methylene compound, could also enable alkylation (Table 3, entries 7 and 8). It's worth noting that diethyl 2-(3-chloropropyl)malonate, a useful intermediate of synthetic melotonin, was selectively synthesized by the reaction of diethyl malonate with 1-bromo-3-chloropropane at 65 °C and gave 87.5% yield (Table 3, entry 5). By contrast, the yield was only 60.2% using NaOEt as base.

Reaction selectivity can be ascribed to three factors. First, although nano-K_2CO_3 had a stronger basic property than normal K_2CO_3 in ethanol, the former was still a weaker base than sodium ethoxide. Thus, the equilibrium constant K_1 was far greater than the

equilibrium constant K_2. Second, the pKa of active methylene compound was greater than that of active methylene compound at α-carbon alkylation. Third, the electronic and steric effects of substitutents led to easier reaction with nano-K_2CO_3 particle to form enolic ion (I) than (II). (Scheme 1). Thus, the monoalkylated product could be selectively produced using nano-K_2CO_3 as base.
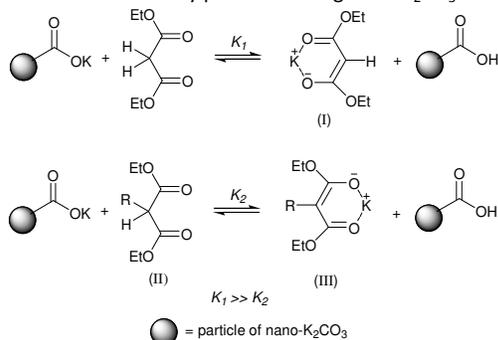
Scheme 1 Equilibrium between active methylene compound and nano-K_2CO_3

Furthermore, the oximation of monosubstituted and nonsubstituted active methylene compounds were examined. Diethyl benzylmalonate was selected as a model substrate for the optimization of oximation conditions (Table 4). Ethyl nitrite, which was slowly generated by the reaction of sodium nitrite with ethanol in the presence of sulfuric acid, was directly introduced into the ethanol suspension solution of nano-K_2CO_3 and diethyl benzylmalonate to give the corresponding oximation product. However, using normal K_2CO_3 as base, no reaction was detected. The reaction conditions were optimized by assessing the amount of base and sodium nitrite(sulfuric acid), reaction temperature and time for obtaining the maximum yield. The yield was improved with temperatures raised. But, boiling point of ethyl nitrite is just 17.4^{o}C, high temperature make ethyl nitrite exist in the form of gas. so the reaction temperature was controlled at 10°C (Table 4, entries 1-4). Increasing reaction time had no significant for improvement of the yield (Table 4, entry 5). Increasing the amount of ethyl nitrite had significant improvement on the reaction(Table 4, entries 6,7). Increasing the amount of nano-K_2CO_3 had significant improvement to the yield in 0.3-0.5 mol (Table 4, entries 9,10). Obviously, this synthetic strategy (Table 4, entry 10) compared with traditional solution protocol[10b] has advantages of high yield, mild reaction condition and simplified work-up process.

Table 4 Optimization of oximation conditions^a

| Entry	Nano-K_2CO_3 (mol)	NaNO$_2$ (H$_2$SO$_4$) (mol)^b	T (°C)	Time (h)	Yield (%)^c
1	0.3	0.2 (0.1)	0	5	69.3
2	0.3	0.2 (0.1)	5	5	75.9
3	0.3	0.2 (0.1)	10	5	80.5
4	0.3	0.2 (0.1)	13	5	70.2
5	0.3	0.2 (0.1)	10	6	80.8
6	0.3	0.25 (0.125)	10	5	85.7
7	0.3	0.3 (0.15)	10	5	89.7
8	0.3	0.4 (0.2)	10	5	89.8
9	0.4	0.3 (0.15)	10	5	91.6
10	0.5	0.3 (0.15)	10	5	94.5
11	0.6	0.3 (0.15)	10	5	94.5

^{a} Diethyl benzylmalonate was 0.2 mol. ^{b} Ethyl nitrite was generated by the reaction of sodium nitrite with ethanol in the presence of sulfuric acid.^{c} Yield of isolated product.

The possible mechanism is represented in Scheme 2. The enolic ion (I) generated by nano-K_2CO_3 reacts with ethyl nitrite to afford nitroso derivative (II). Sequentially, the intermediate (II) is cleaved by ethoxyl anion derived from the ethyl nitrite to form the oximino ester and diethyl carbonate.
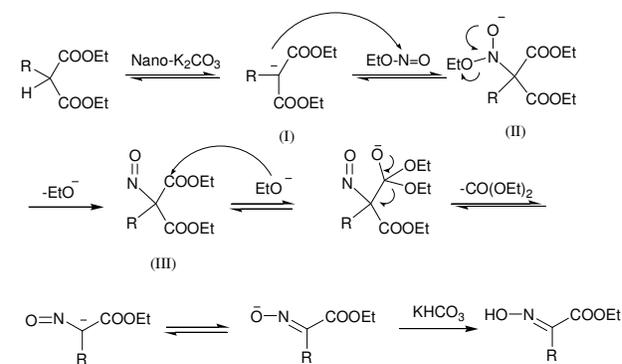
Scheme 2 Possible mechanism of nitrosation reaction

Oximations of various typical β-dicarbonyl compounds were investigated (Table 5). Both monosubstituted and nonsubstituted active methylene compounds could be oximated in good or excellent yields. Arylmethyl (Table 5, entries 1–3) and aryl (Table 5, entry 4) substituted malonic ester could be oximated to afford corresponding products in excellent yields. For dicarbonyl compounds without substituent group at methylene, such as malonate ester and β-ketocarboxylate ester, oximation reactions also smoothly proceeded (Table 5, entries 5–7).

Table 5 Oximation of active methylene compounds
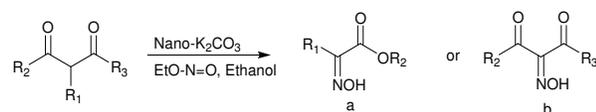
Entry	R_1	R_2	R_3	Product	Yield (%)[a]
1	Bn	OEt	OEt	a	94.5
2	4-Br-Bn	OEt	OEt	a	96.6
3	1-Naphthylmethyl	OMe	OMe	a	87.6
4	C_6H_5	OEt	OEt	a	97.2
5	H	OEt	OEt	b	74.6
6	H	Me	OEt	b	78.4
7	H	4-OMe-C_6H_4	OEt	b	77.8

[a] Yield of isolated product.

After alkylation reaction completion, the mixture of K_2CO_3 and potassium halide were not separated easily. The regeneration of nano-K_2CO_3 used in oximation reaction was carried out. After reaction completion, the filter cake was calcined at 250 °C over 4 h to generate normal K_2CO_3 with yield ≥95%. The normal K_2CO_3 was milled again to generate nano-K_2CO_3 with average particle size of 64 nm. The reaction activity of recovered nano-K_2CO_3 was evaluated through repeating oximation of diethyl benzylmalonate and the yield kept constant when the experiment was carried out repeadly 10 times. Hence, the nano-K_2CO_3 exhibits the same activity within 10 times at least.

Conclusions

In summary, a relatively high activity, low cost, and reusable base nano-K_2CO_3 was developed. The material was endowed with a small average particle size, narrow particle size distribution and strong basicity. Nano-K_2CO_3 can replace sodium ethoxide to complete monoalkylation and oximation of various active methylene compounds in good or excellent yield. Further application of nano-K_2CO_3 will be reported shortly.

Experimental section

General remarks

All commercially reagents were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker Advance II 500 instrument at 500 and 126 MHz, respectively. Chemical shifts were given as δ values (ppm), with tetramethylsilane as internal standard. Coupling constants (*J*) were given in Hertz (Hz). The particle size of nano-K_2CO_3 was measured using a laser particle size analyzer (Zetasizer Nano S90, Malvern Instruments Ltd.). CO_2-TPD was measured with Chemisorb 2720 automatic chemical adsorption apparatus (Micromeritics Instrument Corp). Nano-K_2CO_3 was prepared using GZM-5 High Frequency Resonant Grinding Machine (Beijing More Open Source Technology Development Ltd., Beijing, China) (47.8 Hz) and was observed by scanning electronic microscopy (SEM) performed on a LEO 1530VP instrument.

Preparation of nano-K_2CO_3

Anhydrous K_2CO_3 (150 g), absolute ethanol (63 mL), and lauric acid (0.435 g) were poured into a resonance mill. The mixture was milled at room temperature for 8 h and then directly used for the next reaction.

Typical procedure for the alkylation of active methylene compounds

Diethyl 2-(3-chloropropyl)malonate Nano-K_2CO_3 (1.3 mol, 179.7 g) and a solution of diethyl malonate (1.0 mol, 160.2 g) and 1-bromo-3-chloropropane (1.1 mol, 173.2 g) in absolute ethanol(500 mL) was added to a round-bottomed flask provided with a water-cooled reflux condenser and a thermometer. The mixture was heated to 65 °C on oil bath and stirred for 8 h. The reaction was monitored by GC. The mixture was filtered and distilled to collect the product 205.9 g, yield 87.5%, bp 156-158 °C/16 mmHg; ^{1}H NMR(CD_3OD, 500MHz) δ: 1.29 (t, *J* = 7.0 Hz, 6H), 1.81 ~ 1.87 (m, 2H), 2.01~ 2.06(m, 2H), 3.48 (t, *J* = 7.5 Hz, 1H), 3.63(t, *J* = 6.5 Hz, 2H), 4.19 ~ 4.26(m, 4H); ^{13}C NMR(CD_3OD, 125 MHz) δ: 14.5, 27.2, 31.3, 45.2, 49.3, 62.5, 170.7.

The other monoalkylated products were prepared similarly according to the procedure used for Diethyl 2-(3-chloropropyl) malonate.

Typical procedure for the oximation of β-dicarbonyl compounds

Ethyl 2-(hydroxyimino)-3-phenylpropanoate Nano-K_2CO_3 (0.5 mol, 69.1 g) was added to a solution of diethyl 2-benzylmalonate (0.2 mmol, 50.1 g) in ethanol (200 mL). Then, the mixture was cooled to 10 °C. Then, a solution of sodium nitrite (0.3 mmol, 20.7 g) in water (100 mL) or ethanol (14 mL) was placed in a 500 mL one-port flask. A solution of sulfuric acid (0.15 mol, 15 g) in water (200 mL) and ethanol (10 mL) was slowly added dropwise to generate ethyl nitrite. Ethyl nitrite was introduced into the reactor through a drying tube. Stirring was maintained for 5 h at a low temperature after adding the sulfuric acid solution. The reaction mixture was then concentrated to remove ethanol. Cold water (30 mL) was added to the residue, and solution pH was adjusted to 5 with cold hydrochloric acid (0.5 M). The solution was extracted with ethyl acetate (3 × 50 mL), and the organic phase was dried with anhydrous $MgSO_4$. Ethyl acetate was removed under reduced pressure to yield crude product. Pure product was obtained by recrystallization using ethyl acetate and hexane. Yield: 39.2 g, yellow solid (94.5%). mp 56 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ:1.34 (t, *J* = 7.0Hz, 3H), 4.00 (s, 2H), 4.30 (q, *J* = 7.0 Hz, 2H), 7.22~7.35 (m, 5H), 9.66 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 14.0, 30.5, 61.9, 126.7, 128.5, 129.2 ,135.7, 150.7,162.2.

The other oximes were prepared similarly according to the procedure used for Ethyl 2-(hydroxyimino)-3-phenylpropanoate.

Regeneration of nano-K_2CO_3

After oximation reaction completion, the mixture were filtered and washed with ethanol(3 × 30 mL). The filter cake was calcined in muffle at 250°C for 4 hours to generate normal K_2CO_3 with ≥95% yield. The normal K_2CO_3 was milled again as the procedure of preparation of nano-K_2CO_3. Nano-K_2CO_3 was obtained and the average particle size of the particles was still 64 nm measured by laser particle size analyzer.

Acknowledgements

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Nano-K$_2$CO$_3$ shows higher basicity and could replace sodium (potassium) alkoxide to carry out monoalkylation and oximation of active methylene compounds.