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A consideration on the state of dispersed metal nitrate and carbonate of Group 1 and 2 elements and basicity generation

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Abstract

Dispersion of metal nitrate or carbonate of group 1 and 2 elements onto alumina and successive activation yielded new type of solid base. Temperature programmed decomposition of thus obtained compound revealed that there are two types of surface species, namely bulk metal nitrate or carbonate species and ion-separated species in which metal cations and anions (nitrate ions and carbonate ions) are separated each other. The latter species is the origin of basicity generation.

Keywords: Solid base; Carbonate; Nitrate; Metal salt; TPD; Butene isomerization; Basicity generation

1. Introduction

A combination of metal salt and support is a popular technique to prepare desirable catalyst. Mounted metal salt may be thermally decomposed under air atmosphere to give metal oxide, be reduced under reducing atmosphere or be decomposed directly under inert atmosphere. Supported metal oxide may also be sulfided under H_2S/H_2 atmosphere. Supported metals, metal oxides, metal sulfides and so on are prepared by this technique. Anions of metal salts may be a source of acidity generation as one can see in the case of sulfated metal oxides [1] and supported tungsten oxide [2]. Preparation of such mounted metal salts can be done by an impregnation method in which a suspension of support in aqueous metal salts or an incipient wetness followed by dry-up procedure is involved. States of mounted salts and their decomposition processes may be of interesting to be investigated.

It is well known that Group 2 metal oxides play as a strong solid base catalyst [3], while Group 1 metal oxides have not been recognized as a strong solid base catalyst [4]. This seems curious if we consider the partial charge of oxygen of both groups. Basicity of oxygen may be higher in the oxide of Group 1 elements as seen in Table 1. Solid bases are prepared under inert atmosphere or under high vacuum from their salts such as hydroxide or carbonate. Once the solid base is formed, it can adsorb acidic carbon dioxide and forms carbonate species and looses its basic properties. Equilibrium constant (K_p) of the decomposition of carbonates at 1273 K and the melting point are also tabulated in Table 1 and the temperature dependence of K_p is shown in Fig. 1. It is clear that higher temperature is necessary to remove carbonate species from Group 1 metal oxide and such a high temperature may result in the strong reduction of the surface area of the oxide because of their lower melting point or lower Tammann temperature. If such a difficulty is overcome, highly basic properties may be obtained on the materials prepared from Group 1 metal salts [5].

This paper deals with the dispersion, decomposition and basicity generation of Group 1 and 2 metal nitrate and carbonate.

2. Experimental

Supports used were alumina (JRC-ALO-4, SA = 177 m^2 g^{-1} or NKHD-24, SA = 340 m^2 g^{-1}). Catalysts derived from Group 1 and 2 nitrate and carbonate were prepared by grinding supports with the salts at given weight ratios with a small amount of water. The paste was dried at 383 K overnight. Since the surface areas of supports are different, amount of metal salts loaded is expressed in terms of a surface density, namely 8 cations nm^{-2}. Name of catalysts is expressed as, for example, 8-KNA that means 8 cations nm^{-2} of KNO_3 was mounted on alumina.

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Table 1
Physico-chemical properties of metal cations and K_p of $M_mCO_3 \leftrightarrows M_mO + CO_2$

M	χ_i[a]	Partial charge of oxygen[b]	K_p at 1000 K	M.p. of oxide/°C	M	χ_i[a]	Partial charge of oxygen[b]	K_p at 1000 K
Li	3.0	−0.80	1.91×10^{-4}	1570	Mg	6.0	−0.50	4420
Na	2.7	−0.81	3.88×10^{-10}	1132	Ca	5.0	−0.57	6.64×10^{-2}
K	2.4	−0.85	1.75×10^{-13}	>763	Sr	5.0	−0.59	2.82×10^{-4}
Cs	2.1	−0.87	1.27×10^{-13}	490	Ba	4.5	−0.61	2.20×10^{-6}

[a] $\chi_i = (1 + 2i)\chi$; i = charge, χ = Pauling's electronegativity [7].
[b] Ref. [8].

Temperature-programmed decomposition (TPDe) technique was used to examine the decomposition process of thus obtained catalyst. By increasing the temperature at the rate of 10 K min^{-1}, desorbed gases were monitored by an ANELVA AQA-200 quadrupole mass spectrometer.

A glass, closed recirculation reactor connected to a gas chromatograph (GC) was employed for the isomerization of *cis*-but-2-ene (*cis*-B). Initial pressure of the reactant was 7.3 kPa (50 Torr) and the reaction was performed at 273 K. A 2.5–10 mg portion of the catalyst was used. The catalytic activity was evaluated from the initial rates. Prior to the reactions, the catalyst was evacuated at desired temperatures (typically at 773 K).

3. Results and discussion

3.1. Temperature-programmed decomposition

A typical TPDe profile is shown in Fig. 2 in which peak profiles of 10CsNA and 13KNA are exemplified. In both cases two distinct peaks are observed. When the amount of loading is low, the high temperature branch is weak and by increasing loading amount this peak grows rapidly. Decomposition products are different in both branches. In the high temperature branch, NO and O_2 are the main components and no NO_2 was found, while in the low temperature branch NO_2 is the main component and no O_2 was observed. This means decomposition processes are different for both branches and the precursors of the decomposition are different. From this observation and considering the decomposition temperature of bulk metal nitrates, the high temperature branch can be assigned to the decomposition of agglomerated phase of mounted metal nitrate. Peak position of the low temperature component is almost independent of a sort of metal cations, dependent on the sort of support and the same to those of mounted ammonium nitrate. Thus, we assign this peak as to the decomposition of dissociated free nitrate ions (ion-separated anion).

Alumina supported potassium carbonate (KCA) showed similar tendency. Low temperature branch appeared at around 400 °C and peak top of high temperature branch appeared at around 800 °C. The high temperature branch was increased with the increase of loading amount as in the case of nitrates. The peak temperature is close to the decomposition temperature of bulk potassium carbonate. So, KCA also gives two species; a bulk species and ion-separated species.

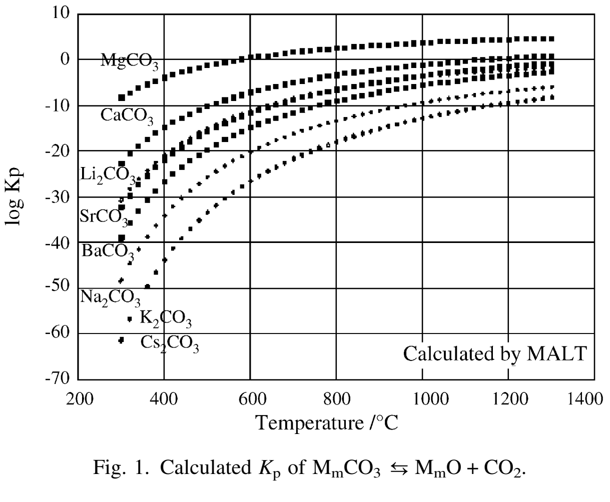

Fig. 1. Calculated K_p of $M_mCO_3 \leftrightarrows M_mO + CO_2$.

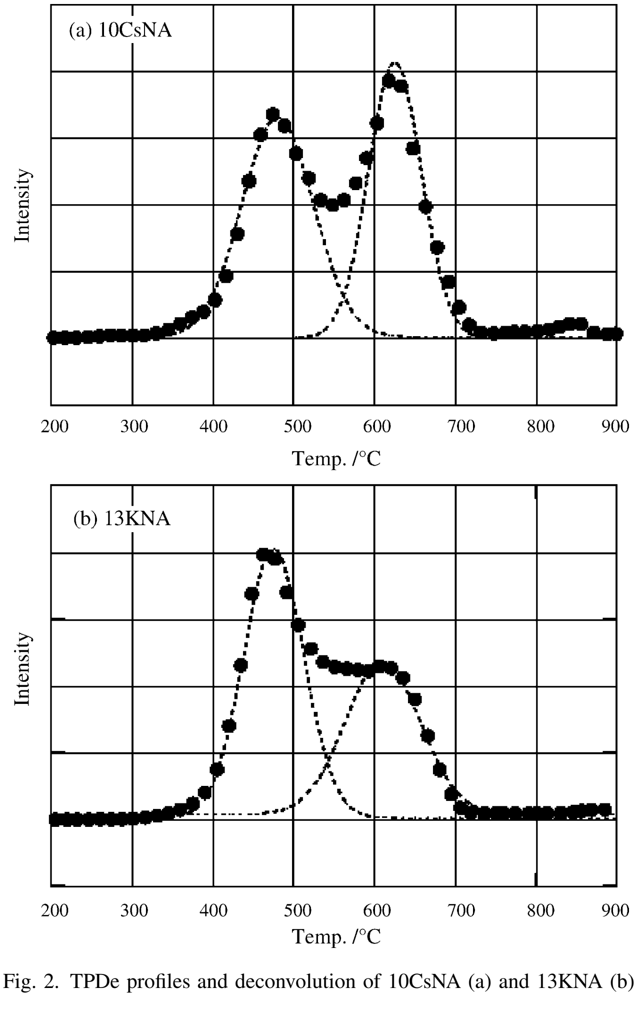

Fig. 2. TPDe profiles and deconvolution of 10CsNA (a) and 13KNA (b).

The origin of these species may be written as follows:

$$\mathrm{M^+X^-(+support)} \leftrightarrows \mathrm{[M^+ + X^-](+support)} \quad \text{in aqueous solution} \qquad (1)$$

After dry-up,

$$\mathrm{[M^+ + X^-](+support)} \rightarrow \frac{\mathrm{[M^+ + X^-]}}{\mathrm{support}} \quad \begin{array}{l}\text{ion-separated species}\\ \text{(decompose at low temperature)}\end{array} \qquad (2)$$

$$\mathrm{[M^+ + X^-](+support)} \rightarrow \frac{\mathrm{[M^+X^-]}}{\mathrm{support}} \quad \begin{array}{l}\text{agglomerated species}\\ \text{(precursor of bulk metal oxide)}\\ \text{(decompose at high temperature)}\end{array} \qquad (3)$$

In an aqueous media, metal salts dissociate to form cations and anions. If the support exists, they are adsorbed individually on the surface of the support (1). During dry-up process, ions may stay as they are when the amount of salts is low (2), while if it is high, ions in the solution agglomerate on the surface (3), the latter being a precursor of bulk metal oxide.

Fig. 3 illustrates the TPDe profiles of 1.5BaNA and 4BaNA. Again when the loading amount becomes high, high temperature branch grows. This phenomenon is reproduced in supported Group 2 metal nitrates. However, the presence of two types of species is unclear from the TPDe profiles of other metal nitrates such as transition metal nitrates. This is because the decomposition temperature of bulk nitrates is low and they decomposed during the preparation procedures or dry-up procedure.

Population of two species can be estimated by applying deconvolution of TPDe profile. Examples are shown in the dotted lines in Figs. 2 and 3. Table 2 summarizes the results of the estimated %population of ion-separated anions and the amount of the ion-separated anions existed on the support. Graphical expression is shown in Figs. 4 and 5. When the surface density increases, %population of anions decreases, while the amount of separated anions gives maximum around 8 cations $\mathrm{nm^{-2}}$, regardless of the sort of cations. This means there is a limited amount of the ion-separated species on the support surface and the maximum amount of ion-separated anions seems to be around 8 anions $\mathrm{nm^{-2}}$ with one exception (KNA). The change of population of separated anions against surface density depends on a sort of metal cation. In BaNA, agglomeration starts at low surface density, while this slowly takes place in MgNA. This phenomenon can be attributed to the difference of ionic radii of cations; $\mathrm{Mg^{2+}}$ is the smallest (0.065 nm) and $\mathrm{Ba^{2+}}$ is the largest (0.135 nm). The amount of imaginary metal nitrate to cover a unit surface area (suspected monolayer coverage) may be the smallest in BaNA and the largest in MgNA, hence the formation of ion-separated species is less favorable in BaNA. The difference in the maximum amount of ion-separated species (Fig. 5) may thus be interpreted in terms of ionic radii of cations.

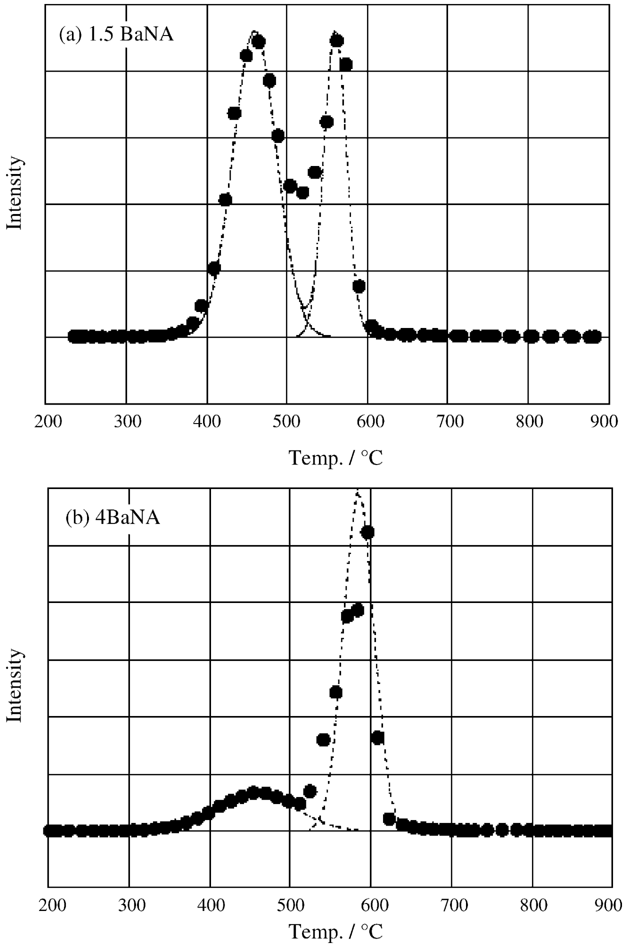

Fig. 3. TPDe profiles and deconvolution of 1.5BaNA (a) and 4BaNA (b).

Although dispersed metal carbonate of Group 1 element gave a bulk species and ion-separated species, ratios of these species were not estimated because the peak profile of low temperature branch was broad, which suggested several ion-separated species were included in this branch. TPDe profiles of the carbonate of Group 2 element show one peak, which suggests there is only one surface species. Since the solubility of Group 2 metal carbonates is low, the ion-separated species is hardly formed during the preparation process. Decomposition of dispersed Group 2 carbonates takes place via bulk metal carbonate.

Decomposition and formation of metal carbonate and nitrate is thermodynamically a reversible process. For instance, when metal cation is free from anions, this may easily contact with NOx at lower temperature under oxidizing atmosphere and forms nitrato species. When the amount of nitrato species is increased, this turns into metal nitrate. By increasing temperature, these species desorb or decompose to liberate NOx species. In other words, cations with weak interaction with support surface can act as a reservoir of NOx species [6]. The situation may be similar in carbonate–$\mathrm{CO_2}$ interconversion.

3.2. Catalytic isomerization of cis-B

Isomerization of *cis*-B takes place rapidly on thus prepared catalysts. Initial but-1-ene/*trans*-but-2-ene (1-B/*trans*-B) ratios

Table 2
%Ion-separated species and their amounts in dispersed metal nitrates

Catalyst	Surface density of cation/ions nm^{-2}	%Ion-separated	Amount of ion-separated anions/ions nm^{-2}
1.5MgNA	1.5	95.8	2.88
4MgNA	4.0	72.8	5.82
8MgNA	8.0	44.6	7.13
12MgNA	12.0	18.1	4.34
1.5CaNA	1.5	100.0	3.00
4CaNA	4.0	66.9	5.35
8CaNA	8.0	45.8	7.33
12CaNA	12.0	22.7	4.45
1.5SrNA	1.5	100.0	3.00
4SrNA	4.0	54.3	4.34
8SrNA	8.0	27.9	4.47
12SrNA	12.0	14.0	3.36
1.5BaNA	1.5	65.3	1.96
4BaNA	4.0	24.7	1.98
8BaNA	8.0	18.8	3.01
12BaNA	12.0	10.9	2.62
8NaNA	8.0	65.8	5.26
4KNA	4.0	100.0	4.00
13KNA	13.0	58.7	7.63
39KNA	39.0	31.9	12.44
10CsNA	10.0	50.6	5.06

are high enough to indicate that the double bond shift (*cis*-B to 1-B) is much faster than the rotation (*cis*-B to *trans*-B), regardless of the catalyst prepared here. Thus, the reaction proceeds via π-allylic anion intermediates that are formed by the proton abstraction from *cis*-B molecule at basic center. The optimum activity was obtained by treatment at a temperature close to that of low temperature branch in TPDe profiles that corresponds to the decomposition of ion-separateed anions.

As is shown in Fig. 6, the reaction rates of *cis*-B, which are estimated from initial conversion and the unit amount of a imaginary metal oxide (excluding support), reach maximum at a surface density of 8 cations nm^{-2} that corresponds to the maximum of the amount of separated anions. Series of KNA and CsNA have the same tendency [2].

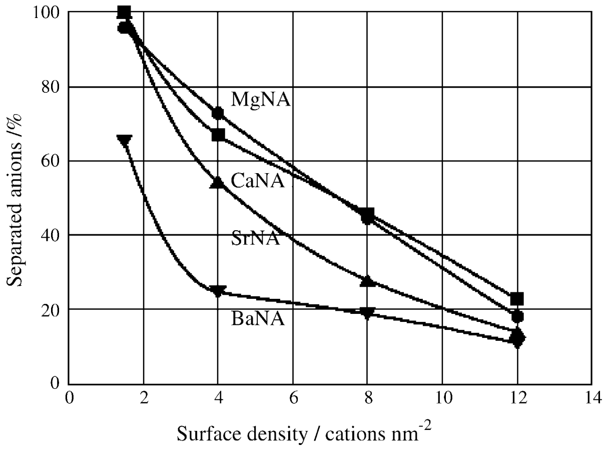

Fig. 4. Change of % separated anion against surface density.

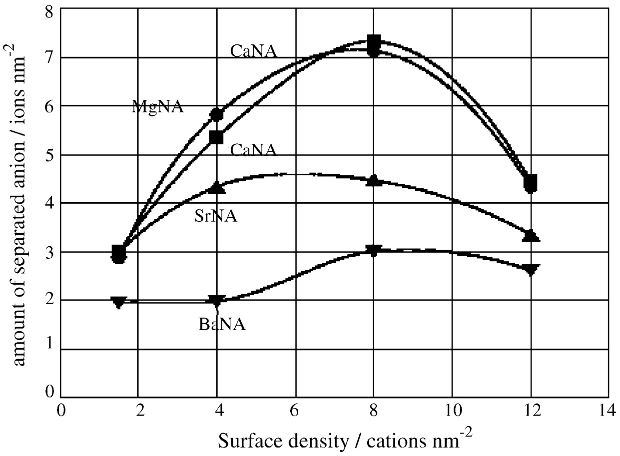

Fig. 5. Change of amount of separated anion against surface density.

Catalytic activity, that was defined as stated above, of Group 1 and 2 nitrate dispersed on alumina is compared in Fig. 7, in which the optimum activity was chosen in each series of catalysts. Activity of Group 1 catalysts is fairly higher than that of Group 2. In the same group, the catalytic activity increased in the order of Cs > K > Na and Ba > Sr > Ca > Mg = 0. The highest activity of 5.82 mol g^{-1} h^{-1} was obtained on 8-CsNA. So, the catalysts derived from Group 1 element can be a strong solid base. As we know the amount of ion-separated species, we can estimate the rate based on this amount. A series of the estimated reaction rate is shown in Fig. 8. Change in thus obtained reaction rate shows the same trend as shown in Fig. 7. The order of activity is Cs > K > Na and Ba > Sr > Ca > Mg = 0.

It is important to point out that (1) the catalyst obtained by the decomposition of Group 1 metal nitrate and carbonate can play as a strong solid base when they were mounted on support such as alumina and decomposed at proper temperature, (2) basicity generation is closely related to the decomposition of ion-separated anions, (3) the ion-separated species seems responsible to the generation of basic sites, and (4) catalytic activity depends on the sort of cations.

In our preceding papers [5], we have proposed the basicity generation as follows. In the low temperature branch, decom-

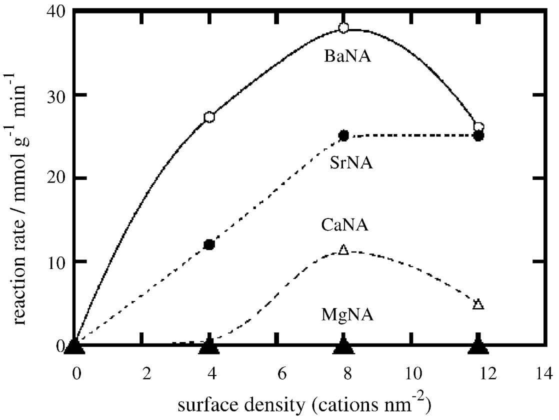

Fig. 6. Change of reaction rate against surface density (based on the unit amount of imaginary metal oxide).

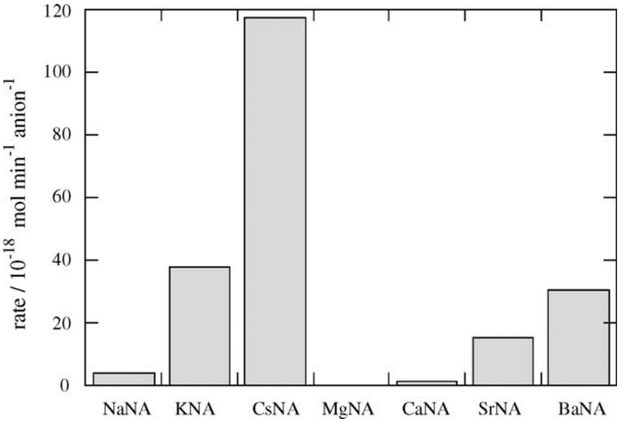

Fig. 8. Comparison of reaction rate (based on the unit amount of separated anions).

position proceeds mainly via Eqs. (4) and (5), and liberated oxygen anions may be a source of a basic center.

$$(M^{+})-CO_3^{2-} \rightarrow (M^{+})-O^{2-} + CO_2 \quad (4)$$

$$(M^{+} \quad \text{or} \quad M^{2+})-NO_3^{-} \rightarrow (M^{+} \quad \text{or} \quad M^{2+})-O^{-} + NO_2 \quad (5)$$

In the high temperature branch, decomposition proceeds mainly via Eqs. (6) and (7). In the equations, M_2CO_3 and MNO_3 denote bulk or crystallized phase carbonate or nitrate. Since no liberation of oxygen anions by this reaction, no generation of basicity should be observed. M_2O could act as solid base, but its contribution may be low since thus obtained metal oxide may have small surface area.

$$M_2CO_3 \rightarrow M_2O + CO_2 \quad (6)$$

$$2MNO_3 \rightarrow M_2O + 2NO + 1.5 \quad O_2 \quad (7)$$

If the ion-separated species are completely free from cations, reaction rates of *cis*-B should be independent of the kind of cations. If the ion-separated species have close contact with cations, cation effect could occur, but it is quite difficult to obtain an evidence of their existence since such species may be a ‘‘cluster metal oxide’’ and hard to identify.

We have obtained a strong solid base from dispersed nitrate or carbonate of Group 1 element, but more investigation is needed for the identification.

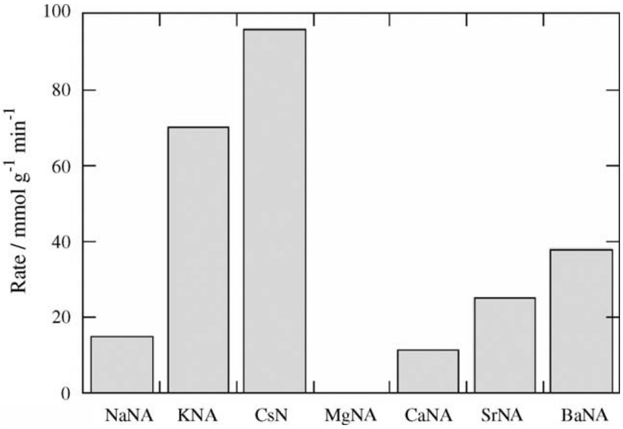

Fig. 7. Comparison of reaction rate (based on the unit amount of imaginary metal oxide).

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