THE REACTIVITY OF DIFFERENT ACTIVE FORMS OF SODIUM CARBONATE WITH RESPECT TO SULFUR DIOXIDE

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The kinetics of the reaction of solid sodium carbonate with sulfur dioxide depends on the microstructure of the solid, which in turn is affected by the way and conditions of its preparation. The active form, analogous to that obtained by thermal decomposition of $NaHCO_3$, emerges from the dehydration of $Na_2CO_3 . 10 H_2O$ in a vacuum or its weathering in air at room temperature. The two active forms are porous and have approximately the same specific surface area. Partial hydration of the active Na_2CO_3 in air at room temperature followed by thermal dehydration does not bring about a significant decrease in reactivity. On the other hand, if the preparation of anhydrous Na_2CO_3 involves, partly or completely, the liquid phase, the reactivity of the product is substantially lower.

A detailed kinetic study of the reaction of anhydrous sodium carbonate with gaseous sulfur dioxide has led to the discovery of two kinetically different forms of Na_2CO_3, viz. active and inactive[1-3]. So far, the active form could only be prepared by thermal decomposition of $NaHCO_3$ under defined conditions[4]. The inactive forms include, e.g., commercial calcinated soda or samples prepared by dehydration of $Na_2CO_3 . 10 H_2O$ via the liquid phase.

Recent investigations revealed[5] that the microstructure of anhydrous sodium carbonate prepared by dehydration of $Na_2CO_3 . 10 H_2O$ in a vacuum at room temperature approaches that of the active form obtained by thermal decomposition of $NaHCO_3$; the specific surface area of the two kinds of anhydrous Na_2CO_3 is nearly the same, viz. about 11 m^2/g. The present work was concerned with the kinetic properties of anhydrous Na_2CO_3 prepared either by dehydration of $Na_2CO_3 . 10 H_2O$ in a vacuum or by its weathering in air at room temperature; the effect of back hydration of the active anhydrous Na_2CO_3 followed by its thermal dehydration on its reactivity was also examined.

EXPERIMENTAL

$NaHCO_3$, anhydrous Na_2CO_3 and $Na_2CO_3 . 10 H_2O$ were of reagent grade purity. Screened fractions 0.25 – 0.33 mm grain size were used for the treatment as well as for the kinetic measurements.

The treatment included dehydration of $Na_2CO_3 . 10 H_2O$ in a vacuum, weathering of $Na_2CO_3 . 10 H_2O$ in air, and thermal decomposition of $NaHCO_3$ and preparation of Na_2CO_3 monohydrate from aqueous solution or from Na_2CO_3 via the liquid phase.

The rate of the reaction of anhydrous Na_2CO_3 with gaseous SO_2 was measured in an integral reactor with a fixed bed as described previously[2,3]; for the purposes of this study, the equipment was somewhat simplified (the circulation conductivity sensor was replaced with glass bead absorbers). The microstructure was investigated by scanning electron micrography (SEM), for which the pulverized samples were coated with a 20 nm gold layer.

RESULTS AND DISCUSSION

The breakthrough curves were expressed in dimensionless variables Y, which is the relative outlet concentration of SO_2, W, which is the degree of stoichiometric loading of the bed (dimensionless time), and M, which is a parameter specifying the working regime of the reactor. These parameters can easily be derived from the primary experimental data[3,6]. The rate constants were evaluated as described previously[3,7].

Figure 1 shows typical breakthrough curves of the various Na_2CO_3 forms (active, inactive, partly active) during their reaction with SO_2 under identical conditions. The active form (curve 4) was prepared by thermal decomposition of $NaHCO_3$, the inactive form (curve 1) was represented by calcinated soda. The morphological structure of the two forms has been studied previously[5]. The active form exhibited a porous structure with an average pore size of 0.10 – 0.14 μm or less and a specific surface area of 11 m²/g. Since the molar volume of anhydrous Na_2CO_3 is only 54.8% with respect to the initial $NaHCO_3$, the porosity of the active form can be expected to be 45.2%. Assuming a cylindrical shape of the pores, the average pore diameter (in m) for a given porosity can be estimated as $d = K / S \rho$, where K is a constant dependent on the theoretical porosity P calculated from the molar volume change (e.g., if $P = 33.3\%$, then $K = 2$; if $P = 50\%$, then $K = 4$), S is the specific surface area (in m²/g) and ρ is the actual density (in g/m³). The calculated average pore diameter of active Na_2CO_3, viz. 0.14 μm (for $P = 50\%$)
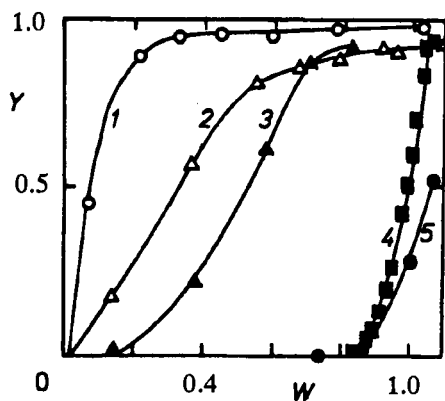

FIG. 1
The influence of the liquid phase during the preparation of the sodium carbonate on its reactivity with respect to sulfur dioxide: $p_{SO_2} = 0.2$ kPa, $T = 423$ K, $M / k = 4.3 . 10^4$, $x_1 = 0.02$ (1), $x_2 = 0.285$ (2), $x_3 = 0.482$ (3), $x_4 = 0.960$ (4), $x_5 = 0.990$ (5). For Y and W meaning see the text

agrees very well with the value estimated by SEM (ref.[5]). It also gives evidence that the thermal decomposition of $NaHCO_3$ is a typical gas–solid process occurring as a topotactic reaction[8]. For the inactive form of Na_2CO_3, on the other hand, microstructure investigation has shown[5] that the particles are not porous, which is consistent with the small specific surface area (less that 1 m^2/g). The microstructure of the inactive Na_2CO_3 (calcinated soda) approaches closely that resulting from the dehydration of $Na_2CO_3 . 10 H_2O$ in air at 105 °C (ref.[5]).

It is therefore reasonable to assume that the morphology of the inactive form establishes completely in the presence of the liquid phase with subsequent precipitation (melting point of $Na_2CO_3 . 10 H_2O$ is 32 °C). During the melting process, the original structure of the sodium carbonate breaks down completely, as has been demonstrated previously[5].

Curve *2* in Fig. 1 concerns sample whose preparation partly involved the liquid phase, viz. so that $Na_2CO_3 . 10 H_2O$ melted in its own crystal water at 55 °C. Curve *3* corresponds to sample prepared by concentrating a saturated solution of Na_2CO_3 by evaporation at 75 °C. Both in this and the preceding cases, preparation of the monohydrate, $Na_2CO_3 . H_2O$, was attempted (the range of its existence is 35.3 – 112.5 °C, ref.[9]); according to chemical analysis, the actual composition was $Na_2CO_3 . 0.6 H_2O$. Comparison of curve *5* (Na_2CO_3 prepared by dehydration of $Na_2CO_3 . 10 H_2O$ in a vacuum at room temperature) with curve *4* (Na_2CO_3 obtained by thermal decomposition of $NaHCO_3$) documents that the samples are kinetically identical active forms with a similar micromorphology[5]. The specific surface area of the sample prepared from the decahydrate is about 10 m^2/g.

On the other hand, samples of Na_2CO_3 whose preparation involved partly or completely the liquid phase (curves *1*, *2*, *3*) exhibit a markedly lower reactivity. For samples to which curves *1* and *2* correspond, the participation of the liquid phase in the development of the Na_2CO_3 microstructure is evident. For the sample prepared by concentrating a Na_2CO_3 solution by evaporation (curve *3*), the lower reactivity as compared with the active form cannot be explained unambiguously. Probably there occurs a transient form of $Na_2CO_3 . 10 H_2O$ or some lower unstable hydrate such as $Na_2CO_3 . 7 H_2O$, which is followed by melting and crystallization of the stable monohydrate. In any case, we assume that if the liquid phase is partly or completely involved, the development of the morphology is different and is associated with a decrease in porosity. The dependence of the reactivity with respect to SO_2 on the way of preparation expressed by the rate constant k and degree of conversion x is shown in Table I.

Figure 2 shows the reactivity of Na_2CO_3 obtained by weathering of $Na_2CO_3 . 10 H_2O$ in air and by dehydration of $Na_2CO_3 . 10 H_2O$ in a vacuum at room temperature. It is clear that the former procedure also results in the active form of Na_2CO_3. The somewhat lower rate constant in this case can be ascribed to the effect of water vapour on the developing morphological structure, characterized by the rate at which the water

vapour is removed from the sample; this rate is somewhat lower than in the process of dehydration in a vacuum.

The effect of back hydration of Na_2CO_3 with water vapour on the reactivity of the active substance is demonstrated in Fig. 3. Samples of active Na_2CO_3, prepared by

TABLE I
The reactivity of the different samples of Na_2CO_3 with respect to gaseous sulfur dioxide (p_{SO_2} = 0.2 kPa, T = 423 K, $M / k = 4 . 10^4$)

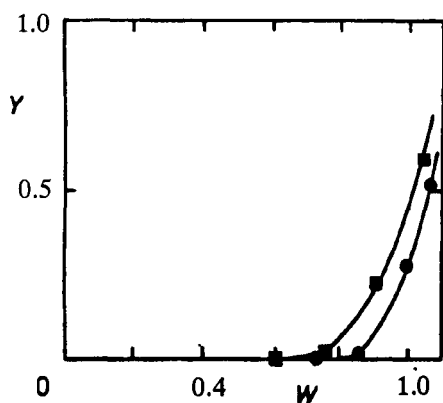| Starting material	Way of preparation	$k . 10^2$, s^{-1} kPa^{-1}	x
$NaHCO_3$ (s)	thermal decomp., 373 K	13.0	0.960
$Na_2CO_3 . 10 H_2O$ (s)	vacuum dehydr., 298 K	8.0 – 10.0	0.990
$Na_2CO_3 . 10 H_2O$ (s)	wheathering, 298 K	7.0	0.959
$Na_2CO_3 . 10 H_2O$ (s)	melting, 328 K	^{a}	0.285
Na_2CO_3, solution	evaporation, 348 K	^{a}	0.482
$Na_2CO_3 . 10 H_2O$ (s)	melting, 373 K	^{a}	0.020

^{a} Rate constant could not be estimated.

FIG. 2
The reactivity of sodium carbonate with respect to sulfur dioxide: p_{SO_2}= 0.2 kPa, T = 423 K, M / k = 4.1 . 10^4, ■ Na_2CO_3 prepared by wheathering of $Na_2CO_3 . 10 H_2O$ at 298 K, $k = 7 . 10^{-2}$ s^{-1} kPa^{-1}, x = 0.959; ● Na_2CO_3 prepared by dehydration of $Na_2CO_3 . 10 H_2O$ in vacuum at 298 K, $k = 10 . 10^{-2}$ s^{-1} kPa^{-1}, x = 0.990. For Y and W meaning see the text
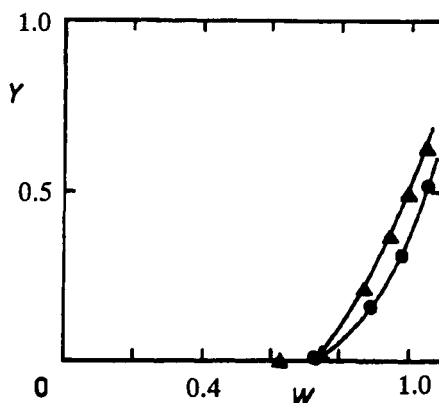
FIG. 3
The influence of the reversed hydration on the reactivity of anhydrous active sodium carbonate with respect to sulfur dioxide: p_{SO_2}= 0.2 kPa, T = 423 K, $M / k = 3.7 . 10^4$; ● Na_2CO_3 prepared by dehydration of $Na_2CO_3 . 10 H_2O$ in vacuum at 298 K, $k = 8 . 10^{-2}$ s^{-1} kPa^{-1}, x = 0.987; ▲ Na_2CO_3 prepared by thermal decomposition of $NaHCO_3$ at 428 K, $k = 7 . 10^{-2}$ s^{-1} kPa^{-1}, x = 0.919. For Y and W meaning see the text

dehydration of $Na_2CO_3 . 10 H_2O$ in a vacuum at room temperature or by thermal decomposition of $NaHCO_3$ at 150 °C, were hydrated in a dessicator over 50% H_2SO_4 under conditions enabling the formation of the Na_2CO_3 monohydrate[10]. Comparison of the reaction courses in Fig. 3 with those for the unhydrated active forms (Fig. 1, curves *4* and *5*; Fig. 2) shows a relatively insignificant decrease in reactivity (a lower rate constant and a lower degree of conversion of the solid). The decrease is more marked for the sample prepared by thermal decomposition of $NaHCO_3$. Still, both samples can be considered active even after the back hydration, whose effect thus is very small.

Dehydration of $Na_2CO_3 . 10 H_2O$ can also be achieved by procedures different from those described. Fig. 4 (*a,b*) shows the different microstructures of inactive Na_2CO_3 (U.S. material – dense soda ash) and of active Na_2CO_3 prepared from the inactive form by crystallization of the decahydrate followed by its dehydration in a dryer under controlled conditions at atmospheric pressure[11,12].

The formation and mutual transformation of the various forms of sodium carbonate are schematically shown in Fig. 5, where "active" Na_2CO_3 is that exhibiting in the reaction with SO_2 degrees of conversion above 90%, "partly active" Na_2CO_3 exhibits degrees of conversion between 10 and 90%, and "inactive" Na_2CO_3 shows degrees of conversion lower than 10%.

CONCLUSIONS

1) Anhydrous sodium carbonate prepared by dehydration of $Na_2CO_3 . 10 H_2O$ at temperatures below 32 °C is virtually as active as that obtained by thermal decomposition of $NaHCO_3$. Also the microstructures and specific surface areas of the two active forms approach each other closely.
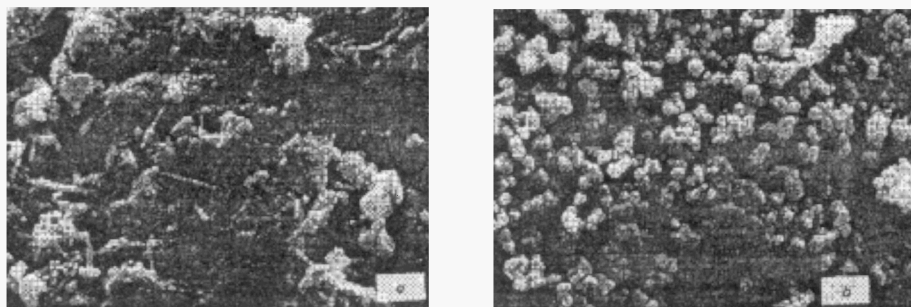

FIG. 4

Microstructure of inactive (*a*) and active (*b*) forms of sodium carbonate (1 bar = 4 μm)

2) Hydration of the active Na_2CO_3, giving the monohydrate, followed by dehydration does not bring about any significant decrease in its reactivity with gaseous SO_2.

3) The reactivity of the anhydrous Na_2CO_3 is considerably lower if the substance has been prepared via $Na_2CO_3 . H_2O$ at temperatures higher that 32 °C; complete dehydration of $Na_2CO_3 . 10 H_2O$ at temperatures exceeding its melting point gives rise to the inactive form whose microstructure is entirely different from that of the active form[5].
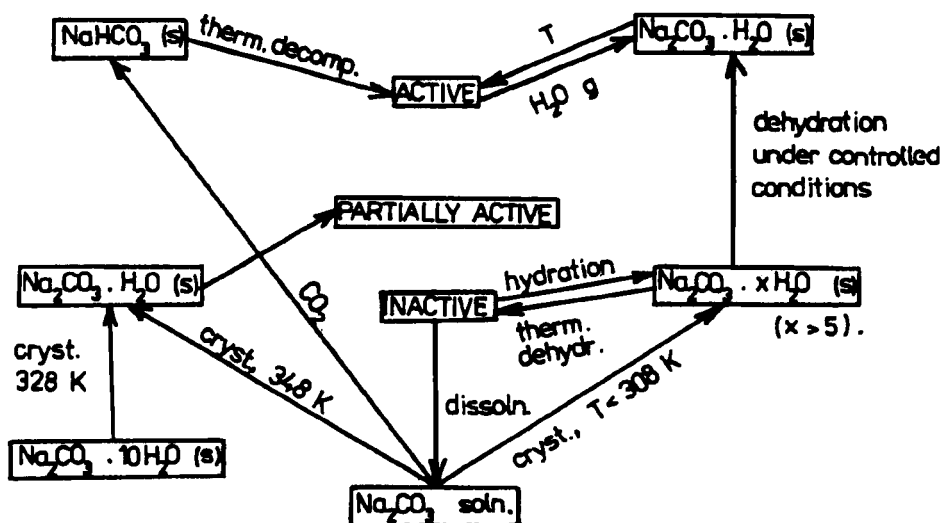

FIG. 5
Formation and transition scheme of the individual forms of anhydrous sodium carbonate

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Translation revised by P. Adámek.