THE EFFECT OF PARENT SUBSTANCE GENESIS ON THE REACTIVITY OF ACTIVE SODIUM CARBONATE TOWARDS SULPHUR DIOXIDE

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The reactivity of sodium carbonate towards sulphur dioxide was studied in dependence on the effect of genesis of sodium hydrocarbonate as the parent substance of the reacting solid. The reactivity expressed by means of the effective rate constant differed approximately one half of order of magnitude among five various samples. A qualitative correlation has been found between the bulk density of the parent substance and the reactivity of active sodium carbonate prepared thereof. Experimental evidence is given that the effect of genesis of the parent substance is not decisive for the reactivity of the active sodium carbonate towards sulphur dioxide. Henceforth, as the decisive factor for the reactivity of the sodium carbonate the way of its preparation from the parent substance must be considered.

A detailed kinetic study of the reaction between solid anhydrous sodium carbonate and gaseous sulphur dioxide has shown, that anhydrous sodium carbonate exists in two forms which differ one from another by several orders of magnitude from the kinetic point of view[1-4]. The active form of sodium carbonate reacts with sulphur dioxide at an extremely high reaction rate which may be demonstrated by the fact that a contact time between the gas and the solid in hundredths of a second is sufficient to remove more than 99% of the sulphur dioxide present in a stream of gas in concentrations of about 10^3 ppm at 150°C. The inactive form of sodium carbonate reacts very slowly and incompletely, and a degree of conversion of the initial carbonate of about 5% is attained in comparison with 95% or more in the case of the active form under the same conditions. In addition, the formation conditions of the active and of the inactive form have been found. The active form of the sodium carbonate is formed by a thermal decomposition of sodium hydrogencarbonate in a stream of an inert gas or air, under conditions which exclude even the transient formation of the hydrate of sodium carbonate[5]. The inactive form is for example represented by the commercial calcined soda A.G. or by samples prepared in the laboratory by dehydrating sodium decahydrate. It can be said that there is nowadays only one known way leading to the formation of active sodium carbonate, namely the thermal decomposition of sodium hydrogencarbonate or of substances containing the hydro-

gencarbonate ion (*e.g.* trona $Na_2CO_3.NaHCO_3.2 H_2O$) under controlled conditions.

The aim of this study was to ascertain the effect of the way of preparation of the parent substance (*i.e.* of sodium hydrogencarbonate) on the reactivity of active sodium carbonate prepared therefrom in its reaction with sulphur dioxide. The effect of particle size of the active sodium carbonate on its reactivity towards sulphur dioxide will be presented later.

THEORETICAL

The heterogeneous reaction of solid sodium carbonate with gaseous sulphur dioxide, expressed by the equation of the general type

$$A (g) + BC (s) = AC (s) + B (g) \tag{1}$$
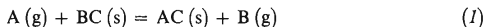
which takes place in an integral fixed bed reactor without any change of the total substance amount, can be described in terms of dimensionless parameters M, Y, and W (ref.[6]). The parameter M is a characteristic quantity, defined by the expression

$$M \equiv kPn_s/F \tag{2}$$

indicating the working regime of the integral reactor. Parameter Y represents the relative outlet concentration of the reacting gas component and is expressed by the relation

$$Y \equiv y_r/y_0 . \tag{3}$$

Parameter W can be characterized as the "degree of the stoichiometric loading of the bed" and is defined as

$$W \equiv y_0 F\tau/n_s = F_g\tau/n_s . \tag{4}$$

The mathematical solution of an integral fixed bed reactor, in which the heterogeneous reaction

$$Na_2CO_3 (s) + SO_2 (g) = Na_2SO_3 (s) + CO_2 (g) \tag{A}$$
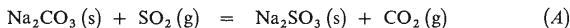
takes place and which is further described by the rate equation

$$r = kpx^{1/2}(1 - x)^{3/2} , \tag{5}$$

leads to a rather complicated relation between dimensionless parameters Y, W, and M (ref.[6]), from which the rate constant k cannot be expressed explicitly. The condi-

tion for a solution in terms of the dimensionless quantities defined by relations (2), (3) and (4), consists in a linear dependence of the reacting gas component expressed by equation (5). An evaluation of the rate constant can be carried out graphically in the following way. From the experimentally obtained dependence of the quantity Y on W, the values of Y are read off for discrete values of the quantity W. The Y vs W dependences for different values of the parameter M have been computed by solving the equation given elsewhere[6], and plotted into diagrams. From these auxiliary diagrams, the values of the parameter M have been read off for a set of experimental $Y-W$ pairs. Subsequently, the value of the effective rate constant k has been obtained from the relation

$$k = M/(M/k),\qquad(6)$$

where (M/k) represents an experimentally determinable quantity. The constancy of the value of the rate constant k for different corresponding $Y-W$ pairs represents a test of the applicability of the mathematical solution of the integral reaction in the given case[6], and simultaneously verifies the validity of the kinetic equation (5).

EXPERIMENTAL

The rate measurements have been carried out in a kinetic apparatus differing from the original arrangement[2] only in the continual recording of the electronic milivoltmeter reading by means of a Kompensograph III recorder (Siemens). The measurements have been carried out with an anhydrous sodium carbonate prepared by thermal decomposition of sodium hydrogen carbonate *in situ* in a stream of nitrogen. In all the measurements, a uniform particle size of 0·25—0·33 mm has been used. The isobaric-isothermal conditions were fulfilled by a small pressure drop along the bed and both by efficient thermostating of the reactor and the high degree of sulphur dioxide dilution in the carrier gas (nitrogen). All measurements were carried out at a temperature of 150°C and at only one level of the partial pressure of water vapour (2·06 kPa). The effects of temperature, carrier gas composition, and of partial pressure of water vapour have been studied previously[3]. Approximately 60 kinetic experiments have been carried out. For the final evaluation of the rate constants, results of 32 experiments have been used, where a material balance varying within the limits of ±2% has been achieved.

Precipitated NaHCO₃ has been prepared by saturating sodium carbonate solution with carbon dioxide at laboratory temperature. The concentration of sodium carbonate (17% by mass) was selected in order to ensure precipitation of pure sodium hydrogencarbonate.

From the phase diagram of the system[7] Na₂O–CO₂–H₂O at 25°C it follows that for initial concentrations of sodium carbonate lower than 17·5% by mass, solid sodium hydrogencarbonate is in equilibrium with the solution. The precipitated sodium hydrogencarbonate has been separated and dried in a stream of carbon dioxide at laboratory temperature.

The commercial sample of NaHCO₃ A.G. (Lachema, Neratovice, imported) contained considerable amounts of moisture and, therefore, has been dried in air for 24 hours at laboratory temperature.

The recrystallized NaHCO₃ has been prepared from the precipitated sodium hydrogen carbona- by forming a saturated solution at 50°C. Continuous saturation with carbon dioxide was main-

tained both during preparation and subsequent cooling of the solution. The separated sodium hydrogencarbonate was after washing dried again in a stream of carbon dioxide at laboratory temperature.

The inoculated NaHCO$_3$ has been obtained from a sodium hydrogencarbonate solution by gradual cooling from 50°C to 31°C after inoculation with precipitated NaHCO$_3$ (fraction from 0·25 up to 0·33 mm). The initial substance for the preparation of the sodium hydrogencarbonate solution has been a calcined Na$_2$CO$_3$ (A.G.) which has been dissolved in 1·5 l of water at 50°C in such an amount that after saturation with carbon dioxide, a saturated solution of sodium hydrogencarbonate (at 50°C) resulted. While maintaining the saturation with carbon dioxide, the seeds of NaHCO$_3$ have been added to the solution which was subsequently gradually cooled to 31°C during 40 hours. The separated sodium hydrogencarbonate has been sucked off, washed with water, and dried in a stream of carbon dioxide. By this procedure, sodium hydrogencarbonate particles of sizes up to 1 mm were obtained.

The pelletized NaHCO$_3$ was a sodium hydrogencarbonate produced by Deutsche Solvay Werke (FRG) as a commercial product (Natriumbicarbonat, grob, venale) of an average particle size of 1/3 mm, which has been screened to a fraction of 0·25—0·33 mm. According to the analysis, this product contained 97·2% by mass of the NaHCO$_3$.

RESULTS AND DISCUSSION

From the experimental values of P, n_s, F, F_g, and τ, the values of the parameter M/k have been determined, and the degree of stoichiometric loading, W, was computed as a function of time. A circulation conductance sensor[2] continually indicated the integral amount of the unreacted sulphur dioxide. The value of $Y(\tau)$ was calculated by numerical differentiation using the three point method according to the formula

$$Y(\tau) = \frac{1}{2\,\Delta\tau F_g}\left[(n_g)_{\tau+\Delta\tau} - (n_g)_{\tau-\Delta\tau}\right], \tag{7}$$

where the sulphur dioxide amount passing through the reactor in time τ was $(n_g)_\tau$. The time interval $\Delta\tau$ between the two n_g determinations was 30, ev. 20 seconds.

The measurements were carried out at M/k values in the range from $1\cdot73 \cdot 10^2$ up to $8 \cdot 10^2$. The evaluation of the rate constant k, proceeded by employing the fact, shown already previously[6,2], that the value of Y is constant for the condition $W = 1$ and $M > 50$. For this reason all the experimental Y vs W curves have been adjusted by means of the Y value within the range of $0\cdot468—0\cdot497$ to a coordinate value of $W = 1$, and a correction of the experimental values of W has been introduced.

In Fig. 1 three Y vs W dependences are given for three different values of the M/k parameter for a sample obtained by inoculation of a saturated NaHCO$_3$ solution. The partial pressure of sulphur dioxide was practically the same for all cases $(0\cdot2$ kPa). For illustration, values of space velocities, s, and mean contact times τ_g, between the gas and the solid are shown. Nevertheless, the accuracy of these values

is not very high in order of the low accuracy of the bed volume determination. The value of the mean degree of conversion of the solid phase can be computed from the relation

$$\bar{x} = \int_0^W (1 - Y)\, dW, \tag{8}$$

or determined by planimetering the area above the Y vs W curve. The values of $\bar{x}$ given in the legend of figures are valid for an integration within the limits of $W = 0$ and $W = 1$. The final degree of conversion of the solid phase has been always higher in dependence on the stoichiometric excess of the sulphur dioxide fed. The character of the Y vs W curves in dependence on the M/k parameter has been substantially the same even with the remaining four samples of sodium hydrogencarbonate.
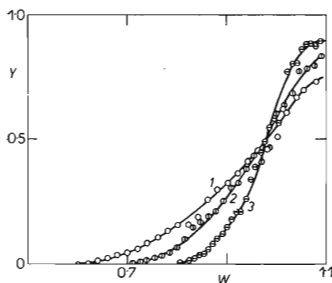

FIG. 1

Effect of the M/k Parameter on the Experimental Y vs W Dependence with the Inoculated Sample at Partial Pressure of Sulphur Dioxide of 0·2 kPa

   1 $M/k = 2\cdot01 \cdot 10^2$, $s = 19\cdot6 \cdot 10^4$, $\tau_g = 9\cdot6 \cdot 10^{-3}$, $\bar{x} = 0\cdot91$; 2 $M/k = 3\cdot86 \cdot 10^2$, $s = 10\cdot4 \cdot 10^4$, $\tau_g = 1\cdot8 \cdot 10^{-2}$, $\bar{x} = 0\cdot93$; 3 $M/k = 6\cdot31 \cdot 10^2$, $s = 6\cdot4 \cdot 10^4$, $\tau_g = 2\cdot9 \cdot 10^{-2}$, $\bar{x} = 0\cdot96$.
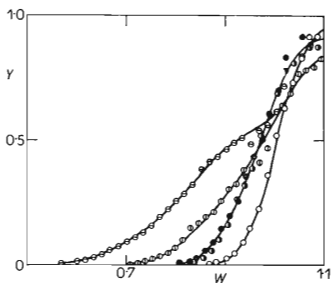

FIG. 2

Effect of the Genesis of Parent Substance on the Reactivity of Active Sodium Carbonate at Constant M/k Parameter

   ○ $M/k = 3\cdot91 \cdot 10^2$, $s = 5\cdot1 \cdot 10^4$, $\tau_g = 4\cdot1 \cdot 10^{-2}$, $\bar{x} = 0\cdot97$, $p = 0\cdot21$ kPa — precipitated sample; ● $M/k = 3\cdot72 \cdot 10^2$, $s = 9\cdot7 \cdot 10^4$, $\tau_g = 2\cdot0 \cdot 10^{-2}$, $\bar{x} = 0\cdot95$, $p = 0\cdot21$ kPa — commercial sample (A.G.); ◑ $M/k = 3\cdot91 \cdot 10^2$, $s = 9\cdot3 \cdot 10^4$, $\tau_g = 2\cdot0 \cdot 10^{-2}$, $\bar{x} = 0\cdot95$, $p = 0\cdot21$ kPa — recrystallized sample; ◐ $M/k = 3\cdot87 \cdot 10^2$, $s = 10\cdot4 \cdot 10^4$, $\tau_g = 1\cdot8 \cdot 10^{-2}$, $\bar{x} = 0\cdot93$, $p = 0\cdot20$ kPa — inoculated sample; ⊖ $M/k = 3\cdot88 \cdot 10^2$, $s = 15\cdot6 \cdot 10^4$, $\tau_g = 1\cdot1 \cdot 10^{-2}$, $\bar{x} = 0\cdot89$, $p = 0\cdot22$ kPa — pelletized sample (FRG).

Fig. 2 shows the Y vs W dependences for the five samples studied at one value of the parameter M/k. The sequence of reactivity of individual samples has been conserved even on changing the M/k parameter both to higher and to lower values.

Fig 3. presents results obtained with the inoculated sample, almost at identical M/k values, however, at different values of the inlet partial pressure of sulphur dioxide. A threefold change of the partial pressure value has no marked effect on the Y vs W dependence within the limits of experimental errors. This finding is in agreement with the assumption of the validity of kinetic equation (5). This conclusion agrees also with previous findings[2] and extends the range of their validity up to a value of the partial pressure of sulphur dioxide of 0·4 kPa (0·4% vol.). The independence of the change of the partial pressure of sulphur dioxide is demonstrated even by the value of the effective rate constant evaluated from the experiments represented in Fig. 3, which assumes the following values: $9·08 . 10^{-2}$, $10·2 . 10^{-2}$, and $8·92 . 10^{-2}$.

A summary of computed values of the effective rate constants of the reaction between sulphur dioxide and active sodium carbonate prepared by thermal decomposition of different samples of the parent substance (*i.e.* sodium hydrogencarbonate) *in situ*, is given in Table I. In addition, the table shows also standard deviations of the rate constant, δ_k, their percentage deviation, and the bulk densities of the parent substance. The value of the rate constant for the precipitated sample is in good agreement with the value published previously[2] for the same sort of sample, $15·75 \pm 3·0 . 10^{-2} \, s^{-1} \, kPa^{-1}$. With samples prepared by dehydrating sodium carbonate decahydrate, it was not possible to evaluate rate constant values, since the reaction took place at rates several orders of magnitude lower. This form of sodium carbonate has been later denoted as inactive soda. The active sodium carbonate prepared by thermal decomposition of the precipitated sodium hydrogencarbonate differs significantly from the inactive form prepared by dehydrating the sodium carbonate decahydrate in the specific surface area. According to measurements carried out
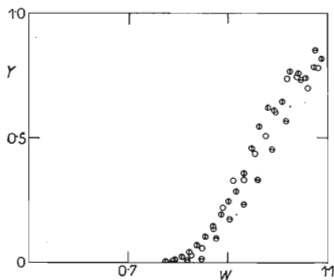

FIG. 3

Effect of the Partial Pressure of Sulphur Dioxide (kPa) on the Character of the Y vs W Dependence with the Inoculated Sample
○ $M/k = 3·84 . 10^2$, $p = 0·13$, $s = 10·1 . 10^4$, $\tau_g = 1·8 . 10^{-2}$; ◑ $M/k = 4·03 . 10^2$, $p = 0·22$, $s = 9·0 . 10^4$, $\tau_g = 2·1 . 10^{-2}$; ◒ $M/k = 4·05 . 10^2$, $p = 0·39$, $s = 9·3 . 10^4$, $\tau_g = 2·0 . 10^{-2}$.

in the Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, by the method of nitrogen adsorption at a temperature of $-198°C$ (the apparatus Sorptomatic, type 1894, Carlo Erba), the active form of sodium carbonate shows a specific surface area of $17.7 \, m^2/g$, whereas, the inactive form $1.1 \, m^2/g$.

Concluding, it can be stated that the active sodium carbonate prepared by thermal decomposition of the parent substance, *i.e.* sodium hydrogencarbonate, exhibits a different reactivity in dependence on the way of preparation or treatment of this parent substance. The difference in reactivity expressed by the value of the effective rate constant k amounted approximately one half of the order of magnitude with five samples studied. A qualitative correlation has been found between the bulk density of the parent substance and the reactivity of the active carbonate prepared thereof. This finding could be of great practical importance for a rapid appreciation of the applicability of the parent substance for preparation of the active form of sodium carbonate.

The kinetic measurements have shown that the effect of genesis of the parent substance for the preparation of sodium hydrogencarbonate is not decisive for the reactivity of the active form towards sulphur dioxide. Henceforth, the proper way of preparation of the active form of sodium carbonate remains the decisive factor. Even with the least reactive sodium carbonate formed by thermal decomposition of the pelletized sodium hydrogencarbonate, a degree of gas purification from sulphur dioxide higher than 99% has been continually achieved up to 70% of the stoichiometric loading of the bed at 150°C. After the stoichiometric amount of sulphur dioxide has been fed, the degree of conversion of the solid phase was higher than 92% at a mean gas contact time of $1.9 \cdot 10^{-2}$ s.

TABLE I

Effect of Preparation of Parent Substance on Effective Rate Constant

Sample	$k \cdot 10^2$ $s^{-1} \, kPa^{-1}$	$\delta_k{}^a$	$\delta_k{}^a$, %	ϱ gcm^{-3}
Precipitated	19.89	± 3.30	± 16.7	0.427
Commercial (AG), imported	12.90	± 3.23	± 24.8	0.720
Recrystallized	12.83	± 1.50	± 11.8	0.748
Inoculated	8.10	± 1.65	± 20.6	0.819
Pelletized (FRG)	3.79	± 1.13	± 28.7	1.158

[a] Standard deviation.

LIST OF SYMBOLS

F total gas feed rate (mol s^{-1})
F_g feed rate of reacting gas component (mol s^{-1})
k effective rate constant $(\text{s}^{-1}\,\text{kPa}^{-1})$
M dimensionless parameter defined by equation (2)
n_s amount of reacting solid substance in reactor   (mol)
p partial pressure of reacting gas component   (kPa)
P total pressure   (kPa)
r reaction rate defined by equation (5)
s space velocity (h^{-1})
y_r mole fraction of reacting gas component in outlet
y_0 mole fraction of reacting gas component in feed
x degree of conversion of reacting solid
$\bar{x}$ mean degree of conversion of solid phase defined by equation (8)
Y variable by equation (3)
W variable defined by equation (4)
τ time   (s)
τ_g mean contact time of gas   (s)
ϱ bulk density (g cm^{-3})

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